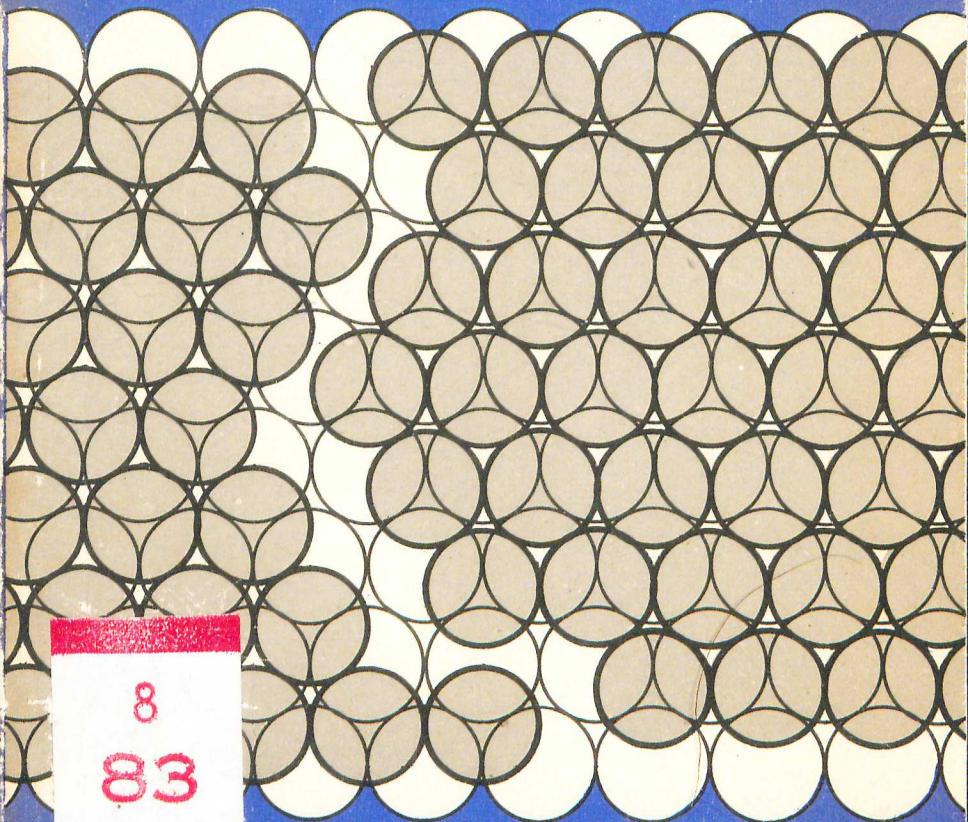


ORDER AND DISORDER IN THE WORLD OF ATOMS

A.I. Kitaigorodsky



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А. И. Китайгородский

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Preface

All bodies surrounding us consist of atoms and molecules. We may wonder how the particles in these bodies are arranged. In disorder, like the many-coloured pebbles on the beach at the seashore? Or in regular order as, for instance, the cells of a honeycomb in a beehive?

One reads in books written twenty or thirty years ago (or, perhaps, even much more recently) that some substances in nature, gases, liquids and amorphous solids, consist of particles in random disorder, while other substances — crystals — have their particles in strict order, arranged by nature in rows and networks.

Is this unconditional statement true of the substances around us? Advances in science have proved this to be wrong. Along with bodies for which the terms *order* and *disorder* are adequate descriptions of the arrangement of their particles, we often find substances in which order and disorder exist together, are inseparable from each other.

The study of elements of disorder in an ordered molecular structure and, conversely, the investigation of elements of order in a chaotic, disordered arrangement of particles have established new and vital laws relating the structure and properties of matter and explaining various phenomena due to changes in the degree of order of its structure. Of equal significance was the study of phenomena associated with transitions from order to disorder and vice versa. Some of today's most important production techniques are based on such transitions.

We can understand the behaviour of a large class of high polymers, so extensively used in our time for synthetic fabrics and building materials and many other purposes, only if we take the peculiarities of their structure into account. Typical of polymers is the simultaneous existence of order and disorder in the arrangement of their various atomic groups. Any changes in the degree of order of molecular chains and their links

lead to drastic changes in the properties of synthetic fibres and plastics.

Of prime importance is the competition between order and disorder in living tissues, and the subject of this book is directly concerned with molecular biology.

Thus, we embark on this study of the structural problems of order and disorder in the world of atoms as a matter of practical interest and not only to extend our knowledge. This is why the author has found it expedient to dedicate a special book to this problem.

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Disorder

Before beginning our discussion of ordered and disordered arrangements of atoms of matter, I want to clarify the concept of disorder by a more simple example. Many readers may feel that the author is forcing an open door since, at first sight, the difference between order and disorder appears to be quite obvious. This is wrong, however, and, strange as it may seem, mathematicians strictly defined order and disorder only some ten or fifteen years ago. They were forced to do this by the advent of electronic computers.

Let us compare two sequences:

1100001101010000001110101000001110011001

In the first place, there is no doubt that both sequences are equally probable. Imagine that you are flipping a coin. Each time it falls heads up you write a zero, and each time it falls tails up you write a one. I am sure you realize by now why all sequences are equally probable. Our series consists of 40 digits. In all, there are two to the fortieth power (2^{40}) different sequences that can be written with forty zeros and ones. What, then, is the distinguishing feature of the first, ordered sequence?

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is impossible to "condense" the instructions; you will have to feed all forty digits into the computer.

It is evident, then, that the degree of disorder can be rigorously determined by the volume of information that you must feed into the computer to enable it to write the required sequence.

Assume that we have written the following sequence:

1010000101000001010000001010000000...

I can say that this sequence is less ordered than a simple alternation of ones and zeros, but it cannot be called disordered. As a matter of fact, my instructions to the computer do not require an enumeration of all the digits that are to be written. It is sufficient to state: write 10 twice followed by zeros, beginning with three and adding one each time.

We can easily miss the elements of order present in disorder, postulating complete disorder where it does not actually exist. Take, for instance, the following sequence of ones and zeros:

10001011101011111000110100010111011101101000

I am not sure you will notice the element of order I have put into this sequence. Nevertheless, it is there: the ones are followed either by one zero or by three. We can readily see that the programmer will be able to condense the instructions he has to feed into the computer, and he has no need to enumerate all the digits in the series.

We have thus found the criterion of disorder. But now you will see that there can be various approaches to the definition of order and disorder in a sequence of ones and zeros. I shall call the disorder discussed above microdisorder.

Hence, microdisorder is a sequence of digits that cannot be condensed when we program the instructions for writing it out. This definition will not essentially differ when we begin discussing atomic structures.

Making use of the same simple example, I shall now demonstrate the concepts of macroscopic disorder and macroscopic order.

The following series is undoubtedly microscopically disordered:

00001110000000111111111000000011110000000000

Nevertheless, I am sure you feel intuitively that some kind of order does exist here. It lies in the fact that we frequently find long sequences of zeros and long sequences of ones. But since these sequences alternate at random and include different numbers of digits, we look for microscopic order in vain.

I shall not present other series of digits, but shall proceed to explain, without further delay, why you have not been deceived by your intuition.

I can write series of ones and zeros, all having complete microdisorder, but differing from one another in the following respect. In some series, consisting of millions of digits, cases of a zero bounded by ones, two zeros bounded by ones, three zeros bounded by ones, four zeros bounded by ones, etc. are found with equal frequency. With the same equal frequency we shall find ones bounded by two zeros, two ones with zeros for neighbours, three ones with adjoining zeros, etc.

If such is the case, we shall contend that the given system of ones and zeros is macroscopically, as well as microscopically, disordered.

We can, however, compile microscopically disordered sequences of another kind. Let us say, sequences in which single ones are rarely found; two ones in succession, more frequently; three ones, still more often; most of the ones are in groups of four; five ones are less frequent; six ones, even less frequent; and the chances of finding fifteen ones in a row are about the same as winning a Rolls-Royce in a lottery. We can say that such a system has macroscopic order and, if necessary, we can describe it by specifying the percentages of ones found in groups of two, three, four, five, etc. in succession.

I expect by now the reader has a clear idea of what is meant by order and disorder, and evidently understands that they can be discussed in two senses: microscopic and macroscopic.

Let us now turn from a consideration of series of zeros and ones to the arrangement of particles in space.

2. Disordered Arrangement of Particles

We shall require the same concepts and the same definitions to clear up the problem of order and disorder in the world of atoms. No need for hurry, however; first we shall investigate the concept of a disordered arrangement of particles. We shall use as an example tiny (point, as the mathematician would say) grains laid out on the squares of a chessboard.

If we occupy only the white squares of the board, or if we place an equal number of grains in each square, or if we place an even number of grains in the squares covered by the move of a knight, then in these and many other similar cases we shall not have complete, or "ideal", disorder.

Now we shall proceed in a different way. We take the bag of grains by its bottom corners and shake out the contents over the chessboard so that the grains are distributed in a single layer. Now they are arranged haphazardly, i.e. at random. If we had to write down the locations of the grains, it would be necessary to specify all their coordinates. We could not condense the information in any way. This is what "at random" means. There is no reason to doubt that we now have ideal microdisorder.

Now we take a thin strip of some definite width, made of a highly transparent material, say plexiglass, and place it in some direction over the board on which the grains have been distributed randomly. A certain number of grains will be under the strip. We count them and obtain, for example, 167. Then we keep changing the position of the strip on the board, counting the number of grains it covers each time. If, in all the counts, we obtain numbers that do not differ much from one another, say 159, 172, 165, 169, etc., we have ideal macroscopic disorder. This indicates that in our collection of grains we have neither especially dense nor especially rarefied rows. The greater the total amount of particles, the less the variation (in per cent) in the numbers of particles (arranged in ideal disorder) that we count under the strip each time we put it into a new position. As we do this, another requirement must be complied with: the results of such counts should not differ essentially, regardless of the point of the strip we pin to the board as the centre of rotation when we turn the strip in different directions. The initial position of the strip is of no significance either.

The criterion of ideal macroscopic disorder just described is called isotropy (from the Greek words *isos*, meaning equal, and *-tropos*, meaning turning; when combined, the word means equal in all directions). A body whose properties are not the same in different directions is said to be anisotropic. If the grains were distributed on the chessboard so that more grains are found under a strip placed along one side of the board than under identical strips perpendicular to the first strip, the distribution of the grains would be anisotropic and, consequently, would not have ideal disorder.

Ideal macroscopic disorder must meet the requirement of constant density of distribution. Let us count the number of grains on any square of the chessboard when they have been poured haphazardly. We shall find approximately the same number of grains on each square. Moreover, if we divide each square

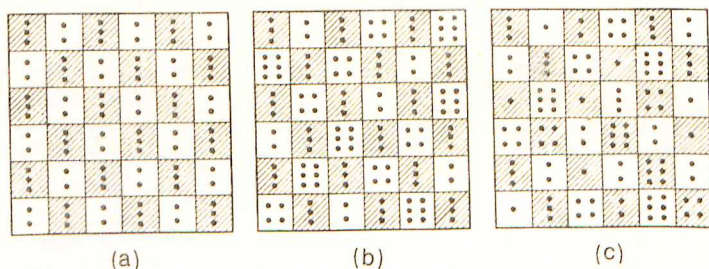


Fig. 1. Grains are scattered on chessboards. (a) Simple arrangement of the grains: two on each white square and three on each black square. (b) More complex order: even numbers of grains on the white squares and the same number on all the black squares. (c) Completely disordered distribution of the numbers of grains on the squares.

of the board into squares of smaller size (but large enough to accommodate many grains), there will still be about the same number of grains on each of the smaller squares. Thus, there will be an approximately constant number of grains, for instance, 10, 9, 11, 12, 8, 10, etc., per unit area of the chessboard. There will be no little squares with too many grains nor any with a negligibly small number. This is what is meant by a constant density of grain distribution.

When we speak of order or of disorder, we must specify the quality of order that we have in mind. All the grains in Fig. 1 are arranged neatly, nevertheless, we use these drawings to illustrate the idea of ordered and disordered arrangements. We are concerned here with order and disorder in the numbers of grains on the squares. We can neatly arrange balls of equal size, but of two different colours, in rows and then discuss the disorder in which the balls are arranged, concerning ourselves with the disorder or order in the succession of the colours.

In the following, we shall be interested chiefly in order and disorder with respect to the geometric arrangement of particles.

3. Gaseous State of Matter

Now we can ask the following question: where, in the world of atoms, do we find ideal macroscopic disorder?

The distribution of molecules in gases is an example found in nature of complete and perfect disorder in the arrangement and motion of particles.

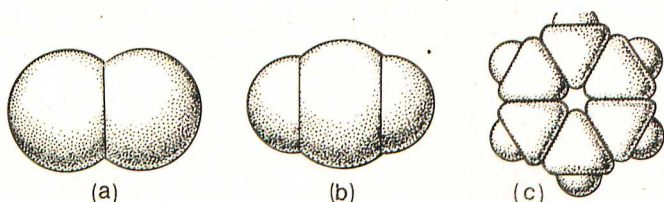


Fig. 2. Models of molecules: (a) oxygen; (b) carbon dioxide; (c) benzene. The contours of the molecules (actually they are far from being so sharply defined, because the density of the matter of the molecule decreases gradually, rather than abruptly as shown) were established on the basis of studies of the close packing of molecules and atoms in crystals.

No microscope exists that would enable us to observe the motion of gas molecules. Physicists, none the less, can describe the behaviour of this invisible world in sufficient detail.

Under standard conditions (room temperature and atmospheric pressure) a cubic centimetre of air contains a huge number of molecules, about 25×10^{18} (i. e. 25 million million million molecules). The volume of air per molecule is about $0.4 \times 10^{-19} \text{ cm}^3$, that is a cube with sides equal to about $0.34 \times 10^{-6} \text{ cm}$. The molecules themselves are very small. For example, the molecules of oxygen and nitrogen, the main components of air, have a maximum size of $0.4 \times 10^{-7} \text{ cm}$ (models of simple molecules are illustrated in Fig. 2). In this typical example, the mean distances between the molecules are about ten times the maximum size of the molecule. The mean volume of gas per molecule is about 1000 times greater than the volume of the molecule itself.

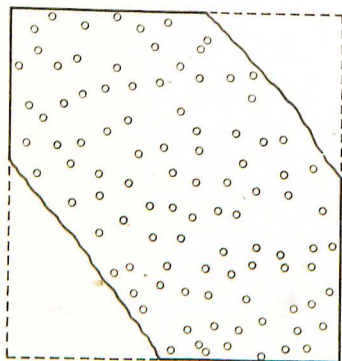


Fig. 3. Dimes randomly scattered over an area of one square metre (plan view). This is approximately the proportion between the sizes of gas molecules and the distances between them.

Imagine a flat piece of ground over which pebbles, the size of a dime, are scattered at random so that there is an average of 100 pebbles per square metre of area. Gas molecules are arranged in approximately the same rare proportion (Fig. 3).

Let us isolate one cubic metre of air under standard conditions. Next we assume that we can determine the density of the air in each half of this volume at any instant of time. Then we shall find that the density and, consequently, the number of molecules in each of the two halves of the isolated volume (under the condition that the halves are separated only mentally) is practically the same. We can continue these measurements, expecting that the eternal disordered motion of the molecules may lead some day to an appreciable difference in the numbers of molecules. It can be proved by theoretical calculations, however, that there is no chance of such a thing happening, even if we continue our measurements for thousand millions of years.

4. Thermal Motion in Gases

Figure 3 schematically resembles a high-speed photograph of a gas. It shows the location of separate gas molecules at some instant.

If such photographs could actually be taken, the exposure would have to be extremely short. The shutter of such a nonexistent camera could be open only for the time it takes a molecule to travel over an almost infinitesimal distance, about $1/10$ of its size. Otherwise, the photograph we obtain would be like one taken in a room filled with dancing couples, using an exposure of several minutes. One-tenth of the size of a molecule is a quantity of the order of 0.1×10^{-7} mm, and the velocity of molecules is about 1000 m (i. e. 1 000 000 mm) per second. Hence, a distance of 0.1×10^{-7} mm is covered at this velocity in 10^{-14} second, i. e. a hundred million millionth of a second.

Is the motion of the molecules fully disordered?

Each gas molecule is in a state of continuous motion. We shall investigate a rarefied, or dilute, gas, in which the interaction of molecules amounts to collisions.

Let us follow the movements of a single molecule. First we see it travelling swiftly somewhere to the right. If there were no obstacles in its path, it would continue in a straight line at the same velocity. But its path is crossed by countless neighbours. A collision is unavoidable, and it occurs. Clash! — and the molecules fly apart like two colliding billiard balls. In which direction does

our molecule rebound; will it gain or lose velocity? Anything can happen; all kinds of encounters are possible. When "attacked" from the rear by a faster molecule, our molecule acquires a higher velocity. A head-on collision slows it down. Side impacts may be from either the right or the left; they may be either heavy or light. It is clear that the molecule, subject to such random collisions, dashes about in the vessel holding the gas.

Sometimes the collisions occur continuously, one after another. In other cases, the molecule succeeds in travelling "peacefully" for comparatively long distances. It may be that the molecule acquires considerable velocity from a series of accelerating impacts, or the opposite may be true: it cannot gain any appreciable velocity owing to a succession of frontal attacks.

If the gas in the vessel does not undergo heating or compression or some other action, its energy remains constant. This energy is the sum of the energies of motion of all the molecules. But we have found that the energy of motion of each molecule keeps changing continuously. How then does the energy of the whole collection of gas molecules remain constant? If one molecule slows down, another one, at the same instant, is accelerated. This means that the relative amounts of slow, medium-speed and fast molecules are retained. Only the affiliation of any certain molecule changes; it may belong to either the fast or slow ones.

How many low-, medium- and high-velocity molecules are there? It would seem, on the face of it, that the percentage of molecules having a velocity, for instance, of 1 to 2 m per second should be equal to that of the molecules having a velocity, say, from 101 to 102 m per second. In the case of complete macroscopic disorder, no particular velocities, we could suppose, should have any advantages. This is wrong, however, as becomes clear when we think of the number of very fast molecules. They would account for all the energy of the gas. This is obviously absurd. It follows that there must be few very fast molecules. Hence, the numbers of molecules having various velocities are not the same. A large share of the molecules in the gas have medium velocities.

In our everyday life cases of medium values are most frequently observed. Buses arrive at your stop in four-minute intervals. The medium, ordinary, most frequent time interval between two successive buses is close to 4 minutes. Intervals of 1 or 2 minutes between buses will be less frequent. Cases in which you have to wait 10 or 15 minutes for a bus are still less frequent. The

greater the deviation from the medium value, the less frequent is the event.

Try to count the numbers of men and women you meet on a busy street during one minute. On an average, these numbers will be the same. The greater the deviation from the average, the less frequently the deviations to either side occur. It is improbable, for instance, that you will meet 100 men in succession. But probability, however great it is, is still not certainty. It should be kept in mind that the average in value does not always coincide with the most frequently occurring event. Such a coincidence is observed only when we can, with equal chances, expect deviations "above average" and "below average".

We are sitting in the grandstand of a race track, watching motorcycle races. The cyclists are driving by at great speed around the track. Assume that we have established that half the motorcycles are racing by at a speed over 130 km per hour, and the other half at a lower speed. We shall call the speed of 130 km per hour the most probable (most frequently observed) speed. If deviations from this speed to either side are due to the skill of the drivers and the proficiency of the mechanics that tuned up the machines for the race, then small deviations to either side occur with equal frequency. In this case, the most probable speed coincides with the average speed. Let us imagine, now, that owing to serious engine trouble, 10 per cent of the drivers drop out of the race and pass by us at a speed of 20 km per hour. The most probable speed remains the same, but the fact that 10 per cent of the motorcycles fail to finish the race substantially lowers the average speed, which is calculated by adding the speeds of all the drivers passing the grandstand and dividing the sum by the number of drivers.

We can compute the average speed of the drivers, we can find the most probable speed, and we can find the percentage of cases in which the speed is so many kilometres per hour less or more than either the most probable or the average speed. We should bear in mind, however, that such computations are of little value when applied to a single event or phenomenon. With all these data available and with a knowledge of the theory of probability, we can come to various conclusions on the distribution of speeds in the race, but we cannot predict the speed at which any definite driver will pass the grandstand. The greater the number of participants in the race, the more accurate the probability estimates that can be made. This holds true for other cases in which probability estimates are applied.

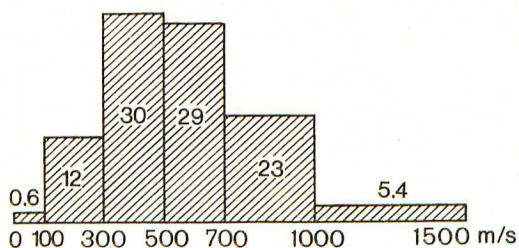


Fig. 4. Velocity distribution for nitrogen molecules at room temperature. The figures (proportional to the areas of the rectangles) indicate the percentage of molecules travelling at the velocities shown in the scale underneath.

We already know how immense the number of molecules is in a cubic centimetre of gas. Under ordinary conditions, this number is about ten thousand million times more than the population of the earth. Therefore, probability assessments are especially precise for molecules.

On the basis of probability theory, physicists computed the numbers of molecules of a gas (in unit volume) having one or another velocity. They found that most of the gas molecules travel at average velocities. Owing to the high number of molecules involved, their average velocity remains constant in each instant of time. Neither is there any change in the relative amounts of molecules having various definite velocities.

Let us consider a numerical example (Fig. 4). At a temperature of about 15°C , the most probable velocity of nitrogen molecules is about 500 metres per second; 59 per cent of the molecules travel with average velocities from 300 to 700 metres per second. Only 0.6 per cent of the molecules have low velocities, from 0 to 100 metres per second. Very fast molecules, with velocities over 1000 metres per second, constitute only 5.4 per cent. The distribution of molecular velocities was first theoretically computed by James Clerk Maxwell (1831-1879), the eminent Scottish physicist.

The disordered, or random, motion of gas molecules arises from the fact that an equal number of molecules are travelling in any direction at any instant and that most of the molecules have a velocity close to the average value.

How often do molecules collide and what distance do they manage to cover without a collision? In this respect too we can only deal with average values because the mean free time, i.e. the time for the mean free path from one collision to the

next, varies within wide limits. There is no regular relationship, of course, between two consecutive mean free paths.

The mean free time and mean free path depend upon the size of the molecules and the density of the gas. The larger their size and the number of them in the vessel, the more frequently they collide with one another. Computations indicate that the mean free path without collisions, under standard conditions, is equal to 0.1 micron for hydrogen and to 0.05 micron for the much larger oxygen molecule. A distance of 0.1 micron, one ten-thousandth of a millimetre, is an extremely small value, but, compared to the size of a molecule, it is far from small. For molecules, a path of 0.1 micron is as many times greater than their size as a path of 25 metres is greater than the size of a billiard ball.

If the average velocity and mean free path of molecules are known, we can readily calculate the mean free time between successive collisions. For a molecule of hydrogen, it equals 5×10^{-9} second, i. e. five thousand millionths of a second.

Chapter Two

Order

1. Symmetry of a Wallpaper Pattern

We observe many articles arranged in order in nature: honeycomb cells in a beehive, flowers planted by a gardener, and others, but ideal order can best be illustrated by wallpaper, with which we are all familiar.

A number of identical drawings of a plant are shown in Fig. 5. This is the simplest type of wallpaper pattern. It is obtained by simply transferring or shifting the smallest piece which has to be drawn by the artist. To single out such a piece, we draw two lines from any point of the drawing, for instance, the centre of a blossom, to the same points of two adjacent drawings. On these lines, connecting the selected drawing with its two nearest neighbours, we can construct a parallelogram as is done in the illustration. It is quite obvious that if we shift or transfer the parallelogram along the directions of the two initial basic lines over distances equal to its sides, we can obtain the whole wallpaper pattern. This smallest repeated piece is commonly called a unit cell. Depending upon the symmetry of the pattern, the unit cell may be of various shapes (square, rectangle, etc.).

This smallest repeated portion can be selected in various ways. It is evident from the wallpaper pattern that several different parallelograms could be selected, each containing the same parts of the drawing. We emphasize that in the given case it makes no difference to us whether the flower or other picture inside the cell is whole or is divided up by the lines bounding the cell.

It would be a mistake to suppose that after drawing the repeating picture for the wallpaper the artist can always consider his job to be finished. It would be finished if the only way to make a pattern for wallpaper was to add to the given portion another identical portion, shifted parallel to the first along the two initial basic lines. In addition to this simplest

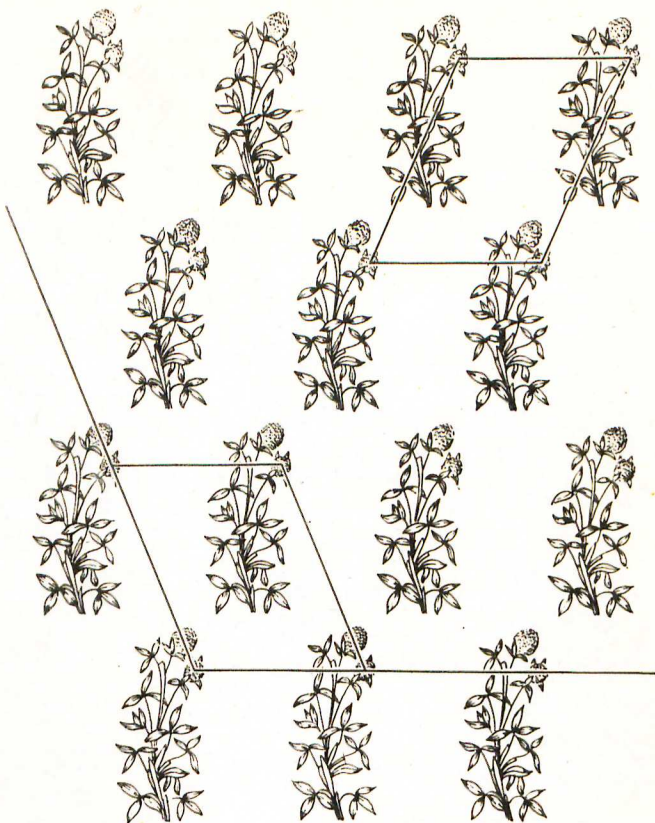


Fig. 5. This simple wallpaper pattern enables us to understand the lattice-type structure of crystals.

method, however, there are sixteen more ways to fill in the wallpaper with an orderly repeated drawing, i. e. there are seventeen types of mutual arrangement of drawings on a plane. They are illustrated in Fig. 6.* The existence of exactly seventeen types of mutual arrangement of drawings on a plane can be proved by geometric methods.

* This illustration has been taken from an extremely interesting book by A. V. Shubnikov called *Symmetry* (in Russian).

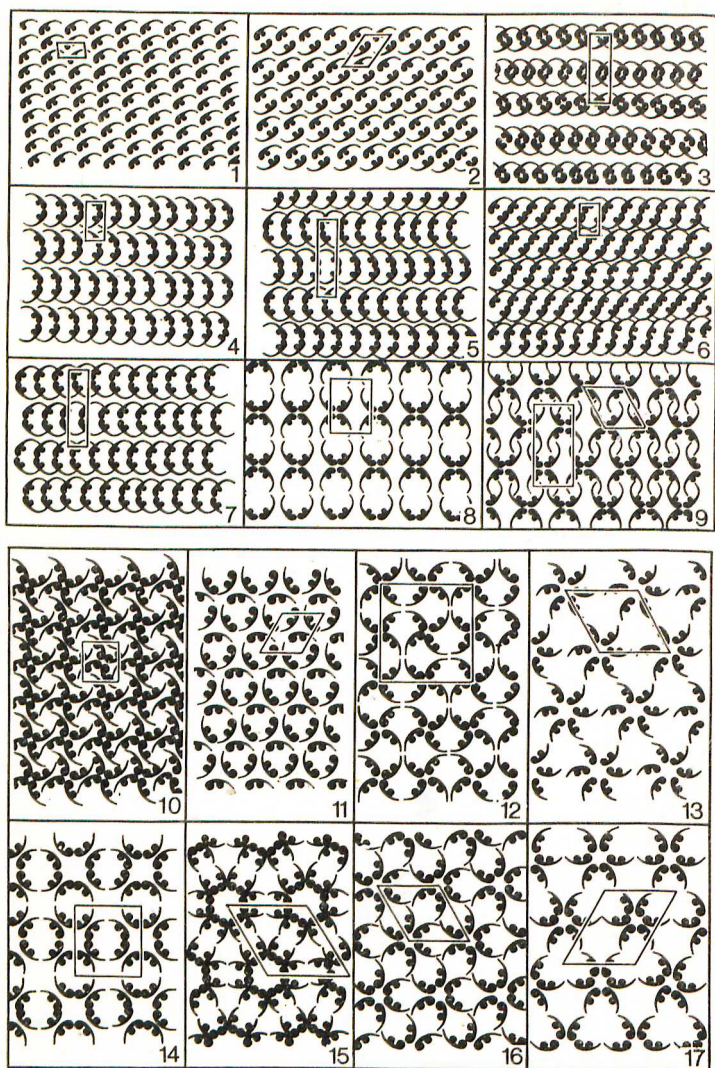


Fig. 6. Seventeen types of symmetry of a plane pattern; the unit cells are indicated by lines.

Here a simpler repeating motif has been selected but, like the one in Fig. 5, it has no symmetry in itself. In the following, the word "motif" will be used to denote this nonsymmetrical blot resembling a comma. The first drawing shows a great number of these "commas" composing the pattern of the simplest kind of wallpaper. All the other drawings are made up of the same motifs, but the patterns composed of them are symmetrical and the difference in the patterns is due to the difference in the symmetrical arrangements of the motifs.

We can see that in the first three cases the pattern has no plane of symmetry: you cannot position a vertical mirror so that one part of the pattern is a mirror reflection of the other part. Cases 4 and 5, on the contrary, have planes of symmetry. Two mutually perpendicular mirrors can be set up in cases 8 and 9. Case 10 has an axis of fourfold symmetry, perpendicular to the drawing. In case 11, the axis is of threefold symmetry, and in cases 13 and 15, of sixfold symmetry.*

Planes and axes of symmetry are found in our drawings in parallel series or families, rather than singly. If you have found one point through which you can pass an axis (or plane) of symmetry, you can readily find the adjacent point and consecutive points, all spaced at the same distance from one another, through which the same kind of axes (or planes) of symmetry can be passed.

Now let us select the smallest portion (unit cell) in these motifs which we can shift parallel to itself over distances equal to the length of its sides and thereby obtain the whole pattern of the wallpaper. In this operation we shall come across several peculiar circumstances.

In the first place, this unit cell may turn out to be a parallelogram (as in case 1 in Fig. 6). Here the smallest portion of the drawing is very small, and we can obtain a clearer idea of the shape of the cell if we mentally prolong its sides. Now we are sure to feel that the angle between the sides does not equal 90° . The unit cell may also be a rectangle (cases 3 and 4), a rhombus with an angle of 60° , and a square.

In the second place, the unit cell contains different numbers of motifs ("commas") in different cases. This number equals 1 for case 1, 4 for case 8, 6 for case 17, etc.

* If a picture coincides with itself after being rotated through a fraction ($1/3$, $1/4$ or $1/6$) of a complete revolution, it is said to have an axis of three-, four- or sixfold symmetry.

It is not always best practice to select the smallest repeated cell in describing symmetrical patterns. The selection of the cell should have a single purpose: to give the clearest idea of the pattern as a whole. In certain cases, however, the smallest (i. e. unit) cell does not meet this requirement.

Let us examine case 9. The drawing indicates a high degree of symmetry in the arrangement of the motifs: the existence of mutually perpendicular planes of symmetry. This high degree of symmetry is not evident if we use the oblique-angled unit cell. Therefore, here, and in all similar cases, a rectangle containing eight motifs is selected as the cell describing the pattern, rather than a unit cell containing only four motifs.

We always have a certain amount of freedom, however, in selecting the location of a unit cell. For instance, it makes no difference whatsoever whether we locate the corners of the cell in the top or bottom of the motifs, or somewhere on the white background between them. The selection of the cell in cases 14 and 15 demonstrates the symmetry of the wallpaper better than, let us say, that of case 8, but this in no way alters the matter. If we wish, we can arbitrarily move the corners of the cell in case 8 without, of course, changing its size and keeping its sides parallel to their initial positions.

The method of filling the unit cell with the motifs differs in each case. This, primarily, is what distinguishes the 17 cases shown from one another. Hence the artist who draws the repeated motif for the wallpaper must indicate, in addition,

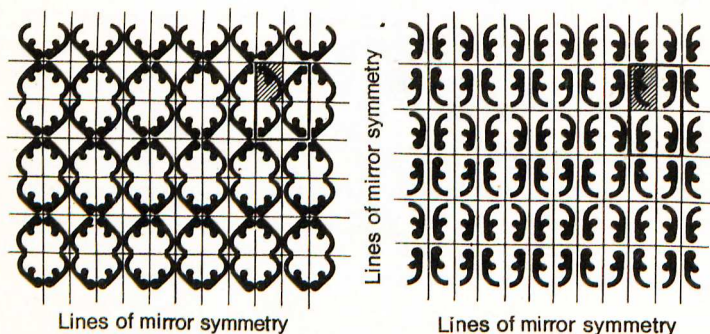


Fig. 7. Two different arrangements of the motifs for the same type of symmetry of the pattern.

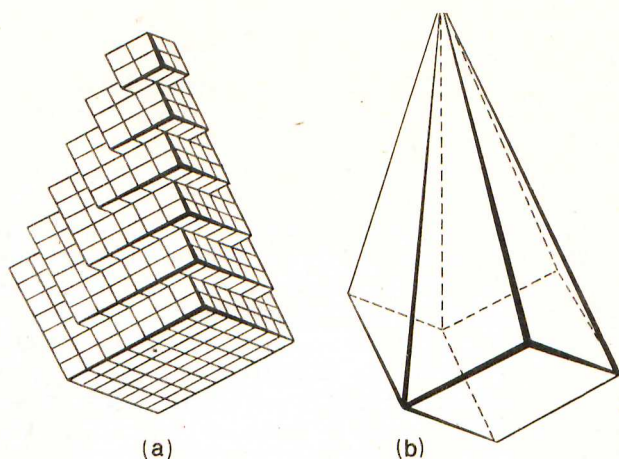


Fig. 8. (a) A model of a crystal consisting of tiny "building blocks".
 (b) A somewhat idealized drawing of a crystal.

which of the 17 methods is to be used to compose the wallpaper pattern from his drawing. In case 8, for example, the drawing he made is to be placed in the hatched part (one-fourth) of the unit cell and reflected in two perpendicular "mirrors" (Fig. 7).

The 17 types of symmetry of a plane pattern do not, of course, exhaust the great variety of patterns that can be composed from a single motif. The artist must specify one more condition: how the motif is to be positioned with respect to the boundary lines of the cell. Figure 7 illustrates two wallpaper patterns with the same initial motif which is differently positioned in each pattern with respect to the intersections of the symmetry planes with the drawing, i. e. lines at which mirrors are located (in a plane pattern, they are simply lines of symmetry). Both patterns come under case 8 in Fig. 6.

We shall not give the rules for composing the wallpaper patterns for all the other cases.

But what has our example of wallpaper patterns to do with crystals?

2. A Crystal

The first scientific views on crystals were expounded as late as the 17th and 18th centuries. An idea of these views is given by Fig. 8, which was taken from a book published in

the 18th century. According to its author, the French mineralogist, Abbé René Just Haüy (1743-1822), named canon of Notre Dame by Napoleon, a crystal is built up of tiniest building blocks, tightly joined to one another. This idea quite naturally comes to mind. Let us break up a crystal of Iceland spar, or calcite (calcium carbonate), with a sharp blow of a hammer. It flies apart into pieces of various sizes. Examining them carefully, we find that the pieces are of regular shape, similar to that of the large crystal, their "parent". Evidently, reasoned Haüy, if we continue to break up the pieces into smaller and smaller ones, we will finally reach the smallest building block, invisible to the naked eye, which is a crystal of the given substance. These ultimate blocks are so small that steps formed by them, which are the faces of the large crystal, seem to be immaculately smooth.

Well, and what is this final building block like?

Investigations in the scattering of X-rays by crystals revealed the "mystery" of the tiniest block. This block, the unit cell of the crystal, consists of a greater or smaller number of atoms, just as the cell of a wallpaper pattern consists of a greater or smaller number of motifs drawn by the artist. A plane of a crystal completely resembles wallpaper. The atoms of which a crystal is built up are arranged along the faces of the crystal like a wallpaper pattern. We could say that a crystal is three-dimensional wallpaper. A crystal is composed by joining tightly together three-dimensional unit cells instead of plane cells as for wallpaper patterns.

How many different ways are there for building up "three-dimensional wallpaper patterns" from these elementary pieces? This complex mathematical problem was solved in 1891 by the founder of structural crystallography, Evgraf Stepanovich Fedorov (1853-1919). He found that there can be only 230 different ways to build up a crystal or, as they say today, 230 Fedorov groups. This discovery of the Russian scientist E. S. Fedorov belongs to the most outstanding achievements of science. Experimental investigations of this theory, begun about 20 years after Fedorov's discovery, led to its convincing confirmation. Not a single crystal has yet been discovered that does not belong to one of Fedorov's 230 groups.

All that is known today about the internal structure of crystals was obtained by X-ray structure analysis, which is based on the optical phenomenon of X-ray diffraction, discovered in 1912 by the German physicist, Max von Laue (1879-1960).

This method consists in putting a small crystal, 0.5 to 1 mm in size, in the path of a narrow X-ray beam. A photographic plate is arranged behind the crystal. Along with the beam passing straight through the crystal, traces of a number of deflected, or scattered, rays are observed on the plate. This phenomenon is known as X-ray diffraction. When the photographic plate is developed, a great number of spots are observed whose arrangement and intensity are indications of the structure of the crystal. The interpretation of such an X-ray diffraction pattern is a complex problem.

The founders of X-ray structure analysis are the English physicist, Sir William Henry Bragg (1862-1942) and his Australian-born son, Sir William Lawrence Bragg (b. 1890).

Since the time X-ray structure analysis was first applied, the structure of many thousands of crystals has been investigated.

3. Invisible Lattices

There are simple crystals which are made up of atoms of a single kind, for example, a diamond which is pure carbon. Crystals of common salt consist of ions (electrically charged atoms) of sodium and chlorine. More complex crystals may be made up of molecules which, in their turn, consist of atoms of many different elements. But the smallest repeated group of atoms (or a single atom in the simplest case) can always be singled out.

In a crystal, as in a wallpaper pattern, we can always find a unit cell, i. e. a parallelepiped whose consecutive transposition, parallel to itself, over a distance equal each time to the lengths of its edges, makes it possible to represent the whole crystal. These lengths are called the lattice constants, or parameters.

The repeating groups of atoms (or single atoms) are arranged in the unit cell with respect to one another in one of the 230 ways predicted by Fedorov.

Crystallographers call the corners of the unit cell lattice points. They are usually associated with the positions of the centres of the atoms in the crystal. Not all the atoms are found, of course, at the corners of the cell. In the least symmetric crystals, the unit cell is an oblique-angled parallelepiped. More symmetrical crystals have a unit cell with the shape, for instance, of a rectangular parallelepiped. The most symmetrical crystals are cubic ones and their unit cell is of cubic shape.

If we attempt to represent the structure of a crystal in space

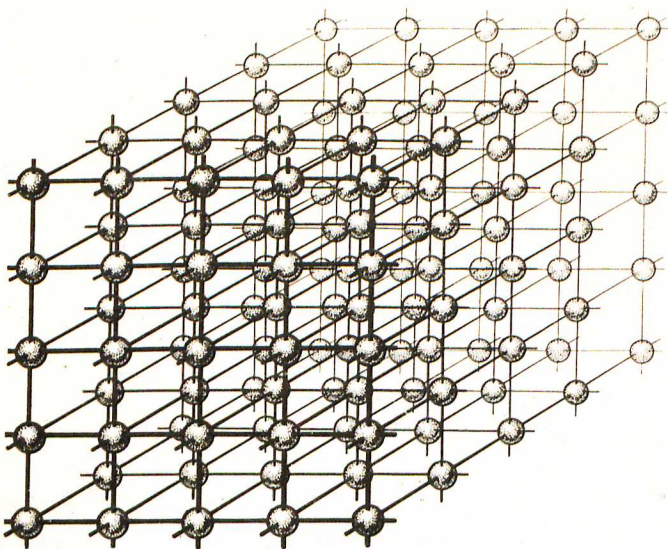


Fig. 9. A model of a crystal lattice. It would be more correct to conceive of the lattice as being incorporeal. Mentally eliminate the wires and leave only the central points of the spheres.

indicating only the points and lines connecting them, we obtain a kind of "skeleton" of the crystal, which is called the crystal or space lattice. Such a skeleton, made of wire with spheres for the lattice points, is illustrated in Fig. 9. The basic feature of crystalline structure is its periodic repetition at strictly equal distances. Suppose we take a "walk" along one of the wires. After leaving a lattice point and starting off along the wire, we would find ourselves in newer and newer locations. But our changing impressions would last only until we reach the next lattice point. From then on we would find a complete repetition of the "landscape" that is already familiar to us from our trip from the first to the second lattice point.

Travelling in different directions inside the crystal, we would observe different patterns. In all cases, however, after travelling a certain distance in a single direction, we would find ourselves in places indistinguishable from those we had already passed, and this would continue to occur after equal intervals.

The size of unit cells varies in a wide range. The shortest distances, 2 or 3 angstroms (a hundred-millionth of a centimetre; $1 \text{ \AA} = 10^{-8} \text{ cm}$), are found, for example, between the lattice

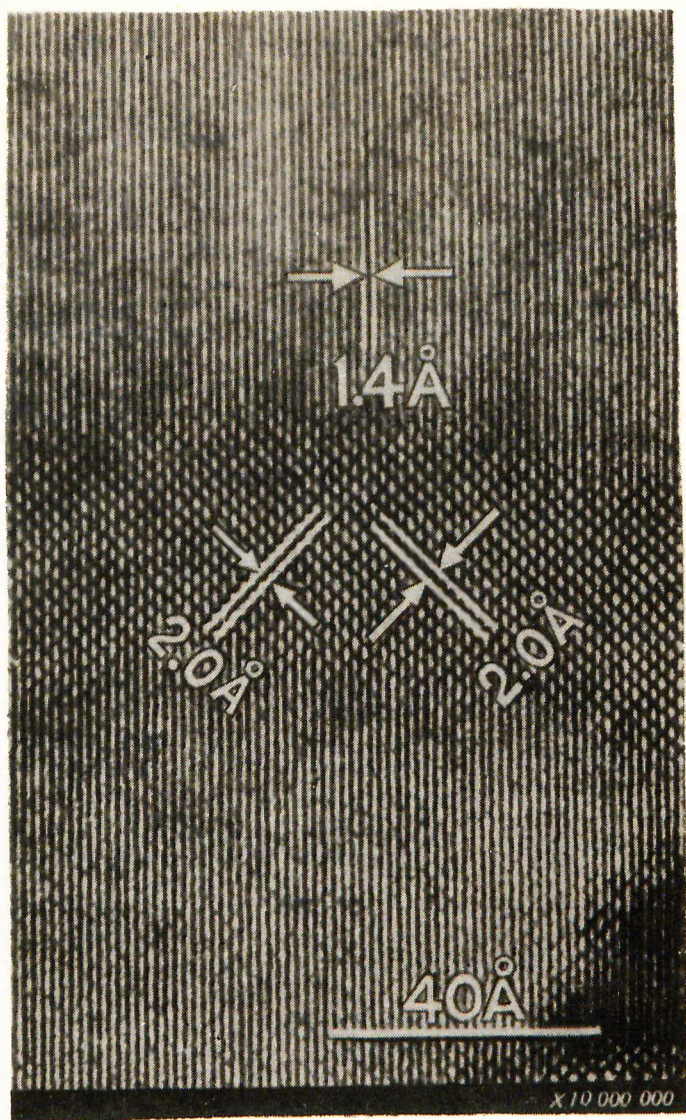


Fig. 10. A photograph enabling the interplanar spacing in the lattice of gold to be measured.

points of the simplest crystals, consisting of atoms of a single kind. The longest distances, up to several hundred angstroms, are found in complex protein crystals, whose separate molecules are large enough to be visible in an electron microscope.

[After rereading this section, written only a few years ago, I thought: isn't it about time to change its title? Look at Fig. 10, which I did not have in the preceding edition. This is an electron-microscope photograph taken with an instrument having record resolving power. The magnification is ten million. Planes at distances of 1.4 and 2.0 angstroms from one another are clearly visible. This is a photograph of gold vapour which formed films on the backing with two different orientations (leading to the two different interplanar distances).

The advance of electron microscopy is truly fantastic. The space lattices of crystals are no longer invisible. The previous name of this section can be justified only by the fact that we see the cross-section of a space lattice and not the whole lattice. This is a flimsy excuse. But the author is so used to praising, in his lectures, X-ray structure analysis as the only method that can be employed to investigate crystals that he cannot bring himself to change the name of this section to a more correct one: Lattices that We See by Means of an Electron Microscope.]

There is a great variety of crystal lattices but the fact that all crystals have certain common properties is due to their lattice structure. To begin with, we can readily understand that the ideally flat faces of a crystal are planes passing through lattice points at which atoms are located. But any number of lattice planes can be passed in the most diverse directions. Which of these planes bound the grown crystal, i.e. become its faces? Let us turn our attention, first of all, to the following circumstance: the population of various lattice planes and lines with lattice points is not equally dense. Experiments show that a crystal is faceted by the planes which are most densely studded with lattice points and that these planes intersect at edges which are also most densely studded with lattice points.

Let us now go over to a discussion of the packing of particles in crystals.

4. Crystals Are Close-Packed Arrangements of Spheres

We know that atoms, the "building material" of crystals, are of extremely complex structure. Electrons, with a negative

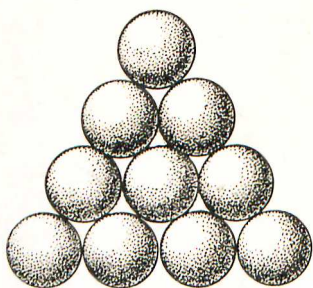


Fig. 11. Billiard balls, set up into a triangle with a rack before beginning a game of pool, are a prototype of the closest packing of identical spheres in a single layer.

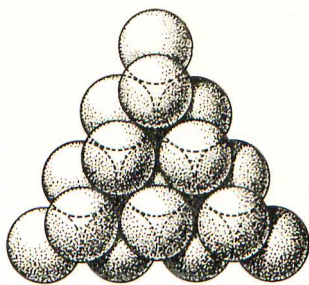


Fig. 12. Two-storied structure of billiard balls. The balls of the second story fit over the white hollows. Now the black hollows form small spaces surrounded by six balls.

charge, rotate at various distances about a positively charged nucleus which, in its turn, consists of many smaller particles.

In very many cases, however (and later we shall indicate the cases referred to here), we can liken atoms to spheres when we wish to represent their arrangement in crystals. This concept of an atom does not by any means fully describe its complex nature. But it correctly shows one important feature of crystals: their structure is based on the closest packing of spheres. This has been demonstrated by X-ray structure analysis of crystals.

To obtain a clear idea of the essence of this principle, we take a large number of billiard balls and arrange them to achieve the closest possible packing. First we can arrange them in the closest possible layer. This looks like that obtained when we set up the billiard balls with a rack into a triangle before beginning a game of pool (pocket billiards), as shown in Fig. 11. When billiard balls are in such a close-packed layer, each ball contacts six neighbours. There is obviously no other way of obtaining the closest possible layer of balls.

To continue our arrangement in space, we shall put layers on top of this first layer. If we stack the balls of the second layer directly above each ball in the first layer, we will not have close-packed balls. To accommodate the greatest number of balls in a certain definite volume, we must place the balls of the second layer in the hollows (triangular open spaces with arcs for sides) between the balls of the first layer (Fig. 12). We should note that we cannot fill all the hollows in the first

layer, only every other hollow, if all the balls are of the same diameter. The hollows in the first layer that cannot be filled have been blacked in in Fig. 12.

There is also only a single arrangement with closest packing in two layers. Of course, we could have put the balls of the second layer in the blacked-in hollows, rather than in the white hollows, but the packing of the balls would not have changed.

There is a difference, however, when we begin the third layer. To obtain closest packing, we must put the balls of the third layer in the hollows of the second layer. But here we have the choice of two possible versions in the stacking arrangement: the centres of the balls of the third layer may be either directly above the centres of the balls in the first layer or above the blacked-in hollows of this layer. Our two three-storied structures both have the same closest packing, but differ essentially.

In making the fourth layer, we further increase the number of possible versions of packing arrangement. From two three-layer arrangements we can make four different four-layer structures. There are eight five-layer arrangements with closest packing, etc. It is obvious that the number of different equally close packing arrangements increases rapidly with the number of layers.

Next we shall show the relation between the closest packing of balls (or spheres) and the crystal lattice. We know that the lattice is built up of little blocks (cells) joined to one another, and that in any direction we choose in the crystal, the structure is strictly repeated after equal intervals. It follows that the crystal is also a packing arrangement of spheres (atoms) in which the position of the spheres in the layers is strictly repeated after a certain number of layers. If repetition begins with the 14th layer, then the cell consists of 13 layers in height. This means that the balls of the 14th layer are directly above those of the first layer, those of the 15th above the second, 16th above the third, etc.

The simplest packing is the two-layer arrangement, with the third layer directly above the first, the fourth above the second, etc. This is the so-called hexagonal close packing. Its lattice (skeleton) is shown in Fig. 13 at the bottom right. In Fig. 13, the positions of the centres of the atoms are indicated by tiny circles, x's and tiny squares. Atoms whose centres are denoted by x's rest in the hollows of both the lower and the

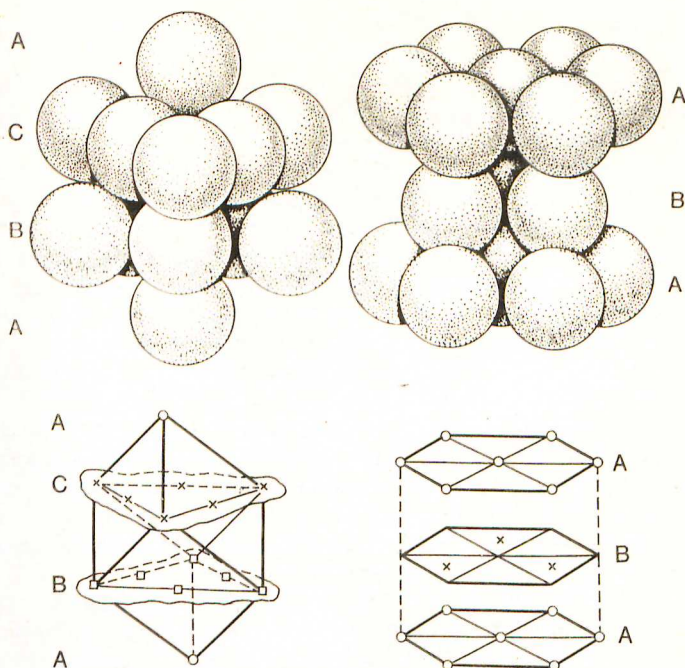


Fig. 13. The architecture of two of the closest packing arrangements for spheres that are most abundant in nature. Both the packing arrangements and their "skeletons" are shown. The centres of spheres which are in the same or repeated layers are indicated by the same symbols.

upper adjacent layers. For example, the crystal of magnesium has this arrangement.

Crystals of the three-layer type, in which the 4th layer repeats the first, the 5th, the second, etc., are very abundant. We can see at the bottom left in Fig. 13, where only the centres of the atoms are indicated, that in such a packing arrangement we can select a cubic unit cell. The dense layers of atoms here are in planes perpendicular to the diagonal of the cube connecting two atoms whose centres are denoted by circles.

Try to imagine a cell positioned so that this diagonal is vertical. The lower atom denoted by a circle will be at the bottom and it will be the only one in our drawing belonging to the first layer (the centres of the other atoms of this

layer, belonging to neighbouring cells, have not been shown in the drawing). The second layer lies closely packed on the first layer. The centres of its six atoms, shown in the drawing, are denoted by small squares located at the vertices and middle points of the sides of a triangle. The third dense layer of atoms is denoted by six x's, similarly located on a triangle. The final, fourth, layer, which repeats the first layer, again consists, in our drawing, of a single small circle.

Hence, the unit cell of a three-layer packing arrangement of spheres is a cube with the centres of the atoms located at its corners and in the centres of its faces. Such a cell comprises what is called a face-centred cubic lattice, which is the type we find in many metals, for instance, aluminium, copper, nickel and, at high temperatures, iron as well.

We now see that a crystal is a system of closely packed particles whose arrangement is repeated in space. The lattice points and the lines connecting these points are simply parts of an imaginary scheme enabling us to recognize a unit cell in the crystal and to visualize the directions in which it must be shifted to fill the whole crystal.

A word about the spheres we have used to represent atoms. Precise measurements by means of X-rays provide the following data: the radii of atoms of various substances vary in comparatively narrow limits, approximately from 0.5 to 2 angstroms.

We have been discussing packing arrangements consisting of identical spheres, i.e. crystals of chemical substances containing atoms of only a single element (true, not all elements are of such simple structure). Now we shall discuss crystals built up of several kinds of atoms, i.e. crystals of compound substances.

Experiments indicate that crystals of very many compound substances can also be represented as closely packed spheres. Atoms of different kinds correspond to spheres of different sizes. Frequently, electrically charged atoms, called ions, serve as the building material of the crystals.

Imagine that we have to pack equal amounts of large and small spheres. How can we obtain the most closely packed arrangement?

Crystallographers found an answer to this question. If we examine the packing of spheres of the same size, we find that not all of the space is filled with the spheres. There are empty spaces between the spheres and we can compute their volume, which turns out to be about one-fourth of the total volume. These empty spaces may be of two kinds. One kind is surrounded

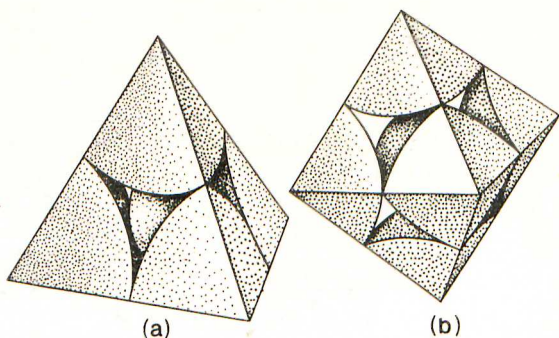


Fig. 14. Structures of crystals made up of atoms of different sizes. (a) A small sphere in the smaller space, or interstice (surrounded by four large spheres). For the sake of clarity, only sectors of the large spheres are shown. (b) Arrangement of a small sphere in a large interstice (surrounded by six large spheres).

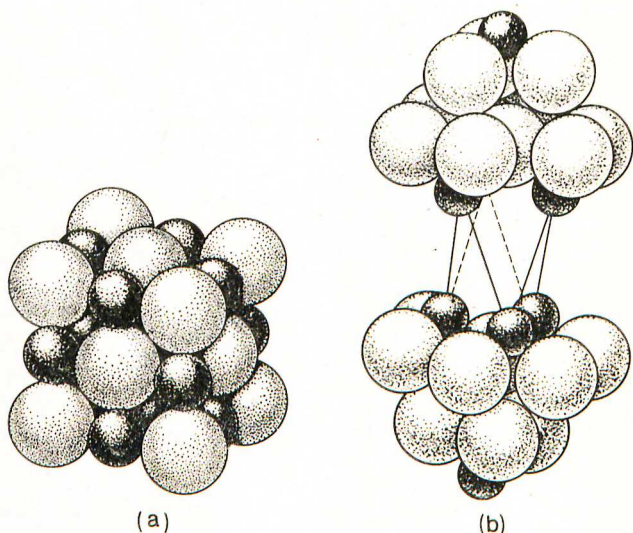


Fig. 15. Ion packing arrangements: (a) in crystals of common salt; (b) in crystals of cadmium chloride. The chlorine ions are larger than the ions of the metals.

by four spheres whose centres are at the corners of a regular tetrahedron (a solid with four triangular faces). The other kind is surrounded by six spheres, with the centres of the spheres forming a regular octahedron (a solid with eight triangular faces). Empty spaces of the first type are smaller in size, and there are twice as many as the second type.

It is clear now how to pack spheres of two different sizes: we first make a closest packed arrangement of the larger spheres and put the smaller spheres into the empty spaces (not necessarily into all of them).

Empty spaces, called interstices, of the two kinds are illustrated in Fig. 14.

It can be computed that for any close packing arrangement of identical spheres, there is one large and two smaller empty spaces per sphere. These empty spaces accommodate small spheres. If they are somewhat large for the space and do not fit in freely, they spread the adjacent large spheres, loosening up the close packing.

Since packing arrangements can consist of different numbers of layers and the pattern according to which the spaces are filled with small spheres can also differ, there may be an immense variety of crystal structures found in nature.

Crystals of common salt are close three-layer packing arrangements of large ions of chlorine (the light spheres in Fig. 15a) with ions of sodium (dark spheres) filling all the large empty spaces. Each ion of sodium is thus surrounded by six ions of chlorine.

Iron sulphide (magnetic pyrite) crystals consist of large ions of sulphur packed in two layers. The smaller ions of iron fill all the large spaces. In a crystal of lithium oxide, chemically composed of two atoms of lithium per atom of oxygen, the close packing arrangement is made up of the large ions of oxygen. The small ions of lithium fill all the small spaces. Therefore, each ion of lithium has four neighbouring ions of oxygen.

In a crystal of cadmium chloride (with two atoms of chlorine per atom of cadmium) the close packing arrangement is formed by the chlorine ions (the large spheres in Fig. 15b). The ions of cadmium, shown by small spheres, fill the large spaces, but not all of them, only the spaces in every third layer of chlorine ions. For the sake of clarity, in Fig. 15b two layers of large spheres, having no small spheres between them, have been removed. The lines show the unit cell of the crystal.

We have shown only the simplest ways of filling up the empty spaces of close packing arrangements.

We should not forget that the representation of atoms by spheres correctly demonstrates one important property of atoms — the possibility of their arrangement in closest packing. It in no way exhausts all the aspects of the complex nature of atoms and it does not imply, of course, that atoms are simply solid spheres. The likening of an atom to a sphere means, in essence, the following. Taking the nucleus of the atom as a centre, we draw an imaginary sphere large enough to contain the main part of the electrons of the given atom. This is the sphere which serves, as they say, as the model of the atom.

The picture of crystal structure described above is not complete unless we add some information on certain features of the behaviour of atoms in crystals.

The point is that when atoms are joined together in a crystal, a part of their electrons are collectivized and belong to the whole crystal rather than to separate atoms. Each of these so-called free electrons no longer moves around within the limits of a single atom all the time, but “roams” throughout the whole volume of the crystal, joining up tentatively with ions it encounters and then leaving them. The basic components of the atoms, i.e. the ions of the crystal lattice, vibrate slightly about their equilibrium positions, in contrast to the chaotic motion of atoms in a liquid or gas. On the contrary, the behaviour of the free electrons of a crystal is, under definite conditions, much like that of atoms in a gas. For this reason, the free electrons are also said to constitute an “electron gas”.

In comparison to the total number of electrons belonging to the atoms, the percentage of free electrons is very small in most cases. This holds true for crystals built up of oppositely charged ions, the crystals of common salt, for instance. Practically all the ten electrons of the positive sodium ion move about near the sodium nucleus, and all the 18 electrons of the negative chlorine ion move about near the chlorine nucleus. (It is necessary to distinguish between free electrons and electrons, one for each atom, which pass over from the sodium to the chlorine in forming the oppositely charged ions. These latter electrons are held tightly by the chlorine, which does not let them go “free”).

It is an entirely different matter in metallic crystals, in which the atoms give up but cannot accept extra electrons. Thus all ions are positive. Here a considerable percentage of the electrons are collectivized. Each atom gives up from one to three electrons for general use from its outer ones, more weakly attracted by the nucleus.

In all monovalent metals, such as lithium, sodium and others, one electron is bound to its atom considerably less strongly than the other electrons. In the crystals of these metals, almost each atom gives up one electron for the common benefit. In bivalent metals, such as calcium, barium and others, approximately two electrons per atom are less strongly bound and are available for the same purpose.

Crystals are formed of atoms owing to the attraction between the atoms. Oppositely charged ions attract each other; for instance, the negative chlorine ions attract the positive sodium ions. Each ion of chlorine attracts six ions of sodium, surrounding itself from "all sides" by particles of the opposite charge. In its turn, each sodium ion attracts six surrounding chlorine ions. This is what leads to close packing of the particles in a crystal.

The attraction of the ions is counterbalanced by their repulsion as they approach one another. The repulsive forces are the forces of interaction between the electrons of the atoms approaching each other. Thus, the ions are spaced in a crystal at a distance at which the attractive forces are balanced by the repulsive forces.

But how about metallic crystals, in which all the ions are positive? Nevertheless, here we also have mutual cohesion of the ions, leading to the formation of a closely packed arrangement. When the atoms come close enough together, a part of the electrons are collectivized as described above. These "common" electrons form a kind of "cement" which secures the ions of the atoms in a close-packed lattice. Closer approach of the atoms is prevented by the electric repulsion of like charges.

5. Crystals Are Not Always Close-Packed Spheres

A great many structures of crystals can be represented as the closest packed arrangement of spheres. Here the atom or ion is attracted with equal force from all sides by neighbouring particles. We can say that the atom or ion behaves as if it were a sphere uniformly coated with glue over its whole surface. There are, however, no fewer structures of crystals for which this simplest of descriptions is unsuitable. The atom behaves like a figure of more complex shape rather than like a sphere. And the "glue" on its surface is applied nonuniformly. Imagine that the "glue" has been applied at only eight spots. Then each sphere will have eight neighbours instead of twelve as in the closest packing of spheres.

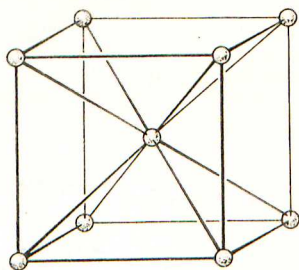


Fig. 16. A body-centred cube. The crystals of many metals have a unit cell of this type.

We should not be surprised, of course, by this departure from the law of closest packing of spheres. On the contrary, it is surprising that the structure of so many crystals obeys this simple rule.

An atom is a complex electrical system. The attractive forces exerted by the atom may be of different value in different directions. The electrons moving around the atomic nucleus may occupy a region having no resemblance to a sphere. Therefore, we find other structures in the world of crystals in addition to those formed by closely packed spheres.

We just mentioned spheres with eight "gluey" spots. This is how atoms of iron (Fig. 16) behave. Iron has a cubic lattice with the atoms located at the corners and in the centres of the cubes. Lithium, potassium, cesium and many other substances have this kind of structure, called a body-centred cubic lattice.

Atoms of mercury behave like flattened spheres. The structure of crystalline mercury is compared in Fig. 17 with that of copper. The latter has a perfect closest packed structure with the symbolic representation ...ABCABC... . As is obvious, both metals have the same characteristic arrangement of the centres of their atoms. But the distances between the layers are less in mercury crystals and the distances between the atoms in a layer are greater. The structure looks as if closely packed spheres were first slightly flattened into thick patties.

"Glue" has obviously been applied nonuniformly to atoms of uranium. Illustrated at the left in Fig. 18 are two layers with the closest packing arrangement: ...ABAB...; at the right are two layers of uranium atoms. The atoms of the upper layer no longer fit in the hollows of the lower layer. The impression we get is that the atoms of the lower layer are "gluey" on the left side, and those of the upper layer, on the right side. This means that the structure of uranium cannot possibly be represented in the form of the closest packing of spheres.

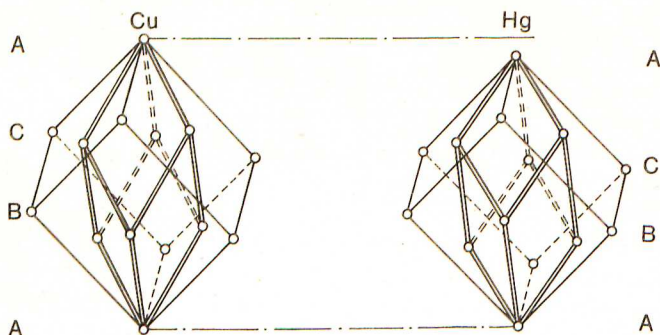


Fig. 17. The crystal structure of copper (Cu) is an example of perfect closest packing of spheres. The unit cell is a cube with an atom at each corner and in the centre of each face. The crystal structure of mercury (Hg) resembles that of copper, except that the distances are different between the atoms in a layer and in different layers.

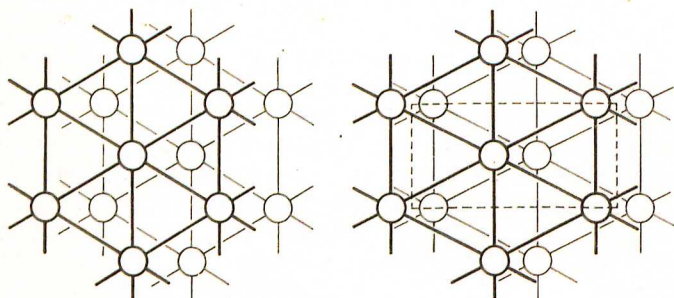


Fig. 18. Here the structure of uranium (at right) is compared with the closest packed hexagonal lattice.

There are a great many examples of such more or less “spoiled” closest packing arrangements. Sometimes the relationship to the packing of spheres is completely lost.

The structure of the diamond is illustrated at the left in Fig. 19. Each atom of carbon has only four neighbours. Obviously, the conception of atoms as spheres does not hold water in this case. If, about the centres of the atoms, we construct spheres of a radius large enough for the spheres to contact one another, 75% of the space in the structure will be empty. Investigations have shown that this is not the case. The atoms of carbon in

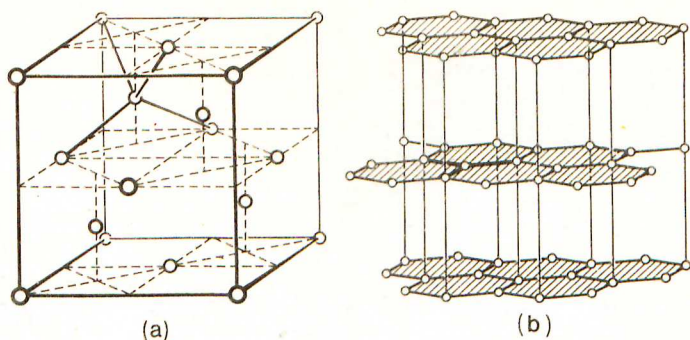


Fig. 19. (a) Crystal structure of diamond, germanium or white tin. (b) Crystal structure of graphite.

the diamond are exceptionally strongly bound together (no wonder they are used to drill rock), and their electronic shells overlap. The binding forces are of a pronounced directed nature, having four directions with an angle of $109^{\circ}30'$ between each pair of forces.

Crystals of silicon, germanium and white tin have a structure closely resembling that of the diamond.

Crystals of ice can be represented by structures consisting of spheres with four "gluey" spots. The bond between each pair of oxygen atoms is provided by a single atom of hydrogen. In the four bonds indicated, there is one atom of hydrogen for each two atoms of oxygen. The structure of ice shown in Fig. 20 has no contradiction, of course, with the chemical formula for water. For the sake of clarity, the hydrogen atoms are shown as binding links, or "necks". Ice has a very loose structure; large "holes" are seen in the drawing. If we assume that the structure is continued above the plane of the drawing, these holes turn into wide channels piercing the structure.

The structure of graphite is shown on the right in Fig. 19, alongside diamond structure. In graphite, the carbon atoms form a layer-type structure. But these are not the layers of closest packed spheres. Try to build up a layer of graphite out of contacting spheres. In the first place, the layer will have a packing with holes and, besides, the adjacent layers will "hang in midair" without being in contact with each other.

As in diamond, there are very strong bonds between the carbon atoms. In contrast to diamond these bonds are at angles of 120° to one another. The atoms of carbon in adjacent layers are about 2.5 times farther away from each other than the atoms

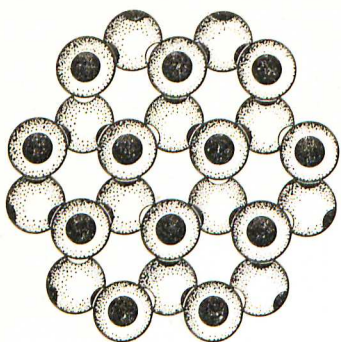


Fig. 20. Structure of an ice crystal (schematic).

in each layer. Naturally, the layers of graphite are bound together incomparably more weakly than the atoms within the layers.

In graphite the layers of strongly bound atoms are flat. Arsenic and phosphorus also have laminated (layer-type) structures in this sense, but the atoms of each layer are not arranged in a plane. In arsenic (Fig. 21), each atom also has strong bonds with three neighbours. As distinct from graphite, here each atom is at the corner of pyramid, and the three atoms bound to it are at the vertices of the base of this pyramid.

As an example of a structure consisting of a chain of strongly bonded atoms, we can mention grey selenium. Each atom of this substance is strongly bonded to only two neighbours. The atoms of grey selenium form an endless helix wound on a straight line. The distances between the atoms of adjacent helixes are

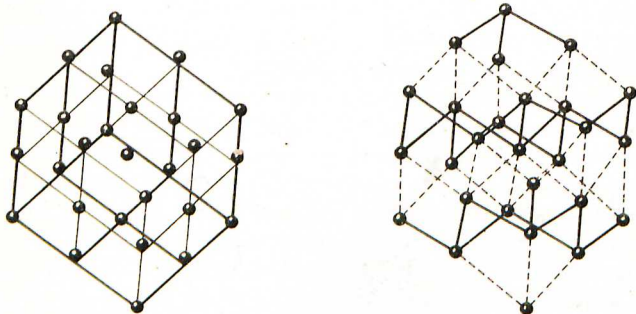
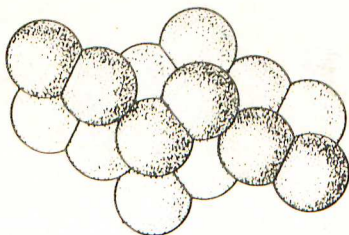


Fig. 21. Atoms of arsenic form layers, which are shown with solid lines in the drawing at the right.

Fig. 22. An example of simplest molecular structure. Diatomic molecules of iodine, as well as molecules of bromine and chlorine are packed in this way.



considerably greater than those between adjacent atoms of the same helix.

Let us now look at Fig. 22. It illustrates the structure of crystalline iodine. Crystalline bromine and chlorine have similar structures.

This time we have shown the atoms in the form of truncated spheres rather than whole ones. By a truncated sphere we mean one with a segment cut off. What do we want to emphasize in this drawing? In the structure of iodine, each atom has only one nearest neighbour. Such a pair of atoms constitutes a molecule of iodine. The binding forces between atoms joined into molecules are greater than the intermolecular forces. The radii of the spheres determine the distances to which various molecules can approach one another. Intramolecular bonds (which are stronger) act as if they flatten the spheres representing the atoms.

We have discussed only a few examples of structures of simple substances. What exceptional diversity! There are crystals having close packed structure in which each atom has equal bonds with its twelve neighbours. In perfect and imperfect close-packed arrangements of spheres, there are no groups of strongly bonded atoms. Yet there are layers of strongly bonded atoms in a graphite crystal and chains of such atoms in a crystal of grey selenium. Finally, there are crystals made up of molecules, groups of strongly bonded atoms.

Such diverse structures are also found in substances consisting of atoms of different kinds. We shall not dwell on the crystals of chemical compounds built of layers and chains of strongly bonded atoms. They are quite scarce.

A typical feature of crystals with a close-packed structure, having atoms of another kind inserted into their empty spaces (interstices), is the absence of molecular formations in the crystal. Let us return to Fig. 15a, which illustrates the structure of a crystal of rock salt. This substance is made up of alternating

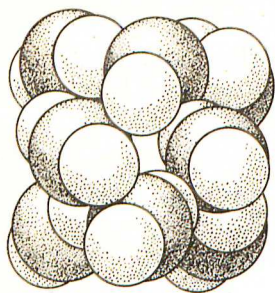


Fig. 23. Close packing of molecules of carbon dioxide. The central atom of the molecule — carbon — is larger than an oxygen atom.

ions of sodium and chlorine. Each ion of sodium has six neighbours, ions of chlorine. All six are arranged in exactly the same way with respect to the sodium ion, and we cannot say that sodium is bonded to any particular chlorine ion. We cannot find any molecules of rock salt, consisting of a single atom of chlorine and a single atom of sodium, in the crystal.

But this is certainly not the case with all crystals. Let us examine, for instance, the crystal structure of carbon dioxide, which exists only at low temperatures. This is the so-called dry ice, obtained by intensive cooling of carbon dioxide that has been liquefied at high pressure.

The crystals of dry ice are built up of molecules. One such molecule is illustrated in Fig. 2*b* (such a representation is conventional, of course, as is the representation of atoms by spheres).

Figure 23 explains how carbon dioxide molecules are packed in the crystal: an atom of carbon has two nearest neighbours: two oxygen atoms. As its nearest neighbour, each atom of oxygen has only a single carbon atom. Close groups of three atoms, the carbon dioxide molecules, are clearly distinguished in the crystal.

In Fig. 2*b* the flattened shape of the spheres constituting the molecule deserves attention. The attractive forces between the atoms of the "trio", i.e. between the carbon and oxygen atoms of a single molecule, are substantially greater than the attractive forces between the various molecules. The electron shells of the carbon and oxygen atoms of a single molecule overlap to a considerable extent, interpenetrating one another. This results from the effect of chemical forces, and suggests the way to depict a molecule of carbon dioxide gas. The interpenetration of electron shells can be represented as flattening of the spheres corresponding to separate atoms. The model of an iodine crystal, shown in Fig. 22, is based on the same principle.

Numerous investigations have established that crystals built up of sphere-like atoms or ions are those of metals, alloys and many inorganic compounds (salts and alkalis). Organic crystals are built of molecules as are certain kinds of inorganic crystals, for instance, those of corrosive sublimate (mercuric chloride). The question is: how are molecules, bodies of complex or even intricate shape, arranged in a crystal?

Just as close-packed sphere structure is produced in ionic crystals by the attraction of the ions, the mutual attraction of the molecules leads to the formation of the closest molecular packing.

The general principle is quite simple: the molecules are arranged so that "projections" of one molecule fit into the "depressions" of another (Fig. 24).

The principle of close packing for molecular crystals leads to the conclusion that it is impossible for structures to exist in which a plane of symmetry would pass between the molecules. In that case, the "projections" of one molecule would be opposite and abut the "projections" of the adjacent molecule. Hence, only definite types of symmetry, 8 to 10 Fedorov groups in all, are possible in molecular crystals. As was shown by the author, it is feasible,

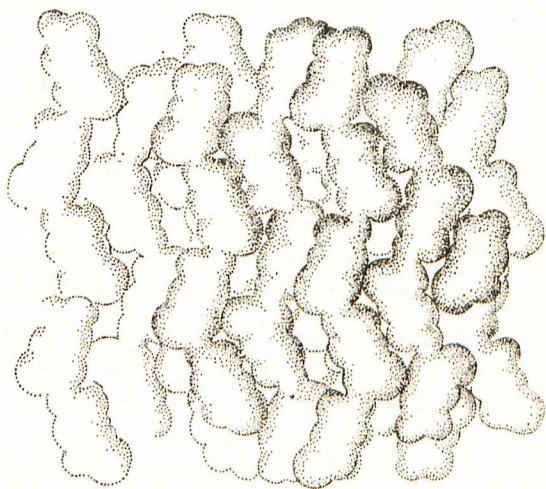


Fig. 24. The principle underlying the structure of crystals of organic compounds. No matter what angles the molecules make with one another, no matter how intricately they are arranged, they still tend to occupy the least volume.

on the basis of close packing, to predict the mutual arrangement of molecules in a crystal, its symmetry and certain other of its properties.

6. The Same Atoms but Different Crystals

The dull black, soft graphite of a lead pencil, with which we can write, and the sparkling, transparent, hard diamond, which cuts glass, are made of the same atoms, namely, atoms of carbon. Why do the properties of two substances, so similar in composition, differ so radically?

If these substances were not crystalline, it would be difficult to explain the existence of two varieties of carbon. But these are crystals and we know that they have different structures.

The lattice of laminated graphite is shown at the right in Fig. 19. Here each atom has three nearest neighbours. In the lattice of diamond, shown at the left, each atom has four nearest neighbours. It is exceptionally clear from this example how distinctly the properties of crystals are determined by the mutual arrangement of their atoms. Graphite is used to make refractory crucibles withstanding temperatures up to two or three thousand degrees, while diamond burns at temperatures above 700°C ; the specific gravity of diamond is 3.5, that of graphite is 2.1; graphite conducts an electric current and diamond does not; etc.

Not only carbon is capable of forming different types of crystals. Almost every chemical element or any substance in the crystalline state has several forms: six for ice, nine for sulphur, four for iron, etc. This is called allotropy, or polymorphism.

At room temperature, atoms of iron form a cubic lattice with the atoms at the corners and centre of the cubes. Each atom has eight nearest neighbours. At high temperatures, iron atoms form a lattice with the closest packing arrangement, and each atom has 12 neighbours. Iron with eight nearest neighbours is soft; that with twelve nearest neighbours is hard. It was found that, in principle, we can obtain iron of the second kind at room temperature by the well-known hardening process (cooling rapidly from a high temperature by quenching in water or oil). Thus, the existence of several forms of the same substance is of immense importance in engineering.

It is evident from the two examples cited above that the different types of crystals of the same substance may have entirely different structures. There are many more examples of this kind.

Thus, yellow sulphur forms puckered rings of eight atoms in a

crystal. In other words, we can see molecules of sulphur consisting of eight atoms in the crystal. Red sulphur also consists of such rings, but they are turned to one another in a different way.

Yellow phosphorus has a cubic structure with eight nearest neighbours. Black phosphorus has a laminated structure resembling that of graphite.

Grey tin has the same kind of structure as diamond. White tin can be obtained from the grey kind if we imagine the diamond structure being squashed flat along the axis of the cube. As a result, each atom acquires six nearest neighbours instead of four.

Several varieties of crystalline structures are also found in organic substances. The same molecules are arranged differently with respect to one another.

7. Long-Range Order

This term can rightfully be applied to the arrangement of atoms in a crystal. In a small crystal, 1 mm in size, the arrangement of the atoms is repeated hundreds of thousands or even millions of times.

Most solids, such as metals and stones, are crystalline bodies. Under ordinary conditions, they consist of crystalline grains, about 0.001 mm in size, that have grown together. But even in such a grain, long-range order is clearly defined, i.e. along the directions of the axes of the cell similar atoms will be found at strictly equal distances hundreds and thousands of times.

Most often, the periodicity of long-range order is equal to two, three or four layers of atoms (or molecules). But exceptionally interesting cases occur when the structure begins to repeat after dozens or even hundreds of layers.

An example of such a substance is silicon carbide, found in nature in various modifications. Occasionally, crystals of silicon carbide are found in which the pattern of the structure is repeated only after 243 layers of atoms (we shall return to this example again on page 134).

The lengths of the periods of repetition, or lattice constants, are very small; in metals they range from 3 to 7 angstroms. In most crystals, the periods do not exceed 20 or 30 angstroms. Long periods, approaching 1000 angstroms, i.e. 0.1 micron, are found in a number of proteins.

Regular repetition of the most intricate structure of proteins has been found after such immense intervals for the world of



Fig. 25. A print of a photograph taken through an electron microscope. The remarkable phenomenon of periodicity in the arrangement of large protein molecules is manifested in the periodic alternation of light and dark bands. The object photographed was a sinew of a bull.

atoms as 0.1 micron in the sinews of a bull (Fig. 25), spines of a porcupine, feathers of a seagull and the tusks of a mammoth. Today the investigators relate the biological peculiarities of tissue and the order and disorder in which its particles are arranged. There is a difference, however, between the order in crystals and in sinews. In the former we are dealing with long-range microscopic order, and in the latter with long-range macroscopic order (see page 61).

8. Order in Finely Crystalline Bodies

The great majority of solids are of crystalline structure. Metals and stones consist of tiny crystals that are visible, for the most part, under a microscope. Grains of sand are concretions of crystals and even clay, if we examine it closely, turns out to be made up of tiny crystals. True, crystals of clay are very peculiar. They permit water to pass between the atomic layers. This is why clay swells so readily. In the kingdom of solids, it is easier to name the noncrystalline substances; they are exceptions. The rule here is a structure of fine grains.

Besides the structure of the crystalline grain itself, of great influence on the properties of solids are the size of the little crystals, their mutual arrangement and the forces binding them together into a single body.

Any treatment of a metal affects its grains. Suppose we have a piece of cast metal. Its grains are arranged in disorder and their size is quite large. Then we make wire of the piece of metal by drawing it through a die. What happens to the metal grains in this operation?

Investigations have shown that a change in the shape of a solid in drawing wire or in some other plastic working technique breaks up the crystalline grains. At the same time, a certain element of order is produced in the arrangement of the crystalline grains by the action of the mechanical forces.

But what possible kind of order can there be here? The fragments of the grains are absolutely shapeless.

This is true: the fragments may be of any random shape, but a fragment of a crystal is still a crystal and the ions in its lattice are packed as regularly as in any well faceted crystal. Hence, we can indicate in each fragment how its unit cells are oriented. Prior to plastic working, the cells are strictly ordered only within each separate grain; there is no total order, as a rule. After the metal is worked, the grains align themselves so that a certain general order becomes evident in their cells. This is called texture. For example, the diagonals of the cells in all the grains become oriented approximately parallel to the direction in which the metal is worked.

Texture is illustrated in Fig. 26*b* by an example of certain definite planes in the grains: the planes most densely filled with ions which are indicated by rows of dots.

Different kinds of plastic working operations (rolling, forging and wire-drawing) produce textures of different types. In some operations,

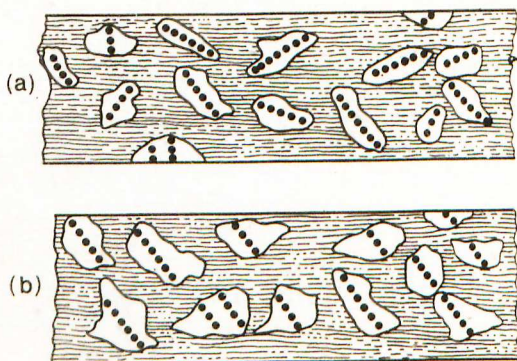


Fig. 26. Absence of a texture (a) and its existence (b).

the grains turn so that the diagonals of their unit cells are aligned along the direction of working, while in others the edges of the cells are aligned, etc. The more advanced the rolling or wire-drawing technique, the more perfect the texture of the crystalline grains of metal.

A texture has a striking effect on the mechanical properties of metal articles. A study of the arrangement and size of the crystalline grains in metals led to an understanding of the essence of the plastic working of metals. This, in turn, led to improvements in the techniques employed.

Another important kind of metal treatment — annealing — is also associated with the rearrangement of metal grains. If rolled or drawn metal is heated to a sufficiently high temperature, new crystals are formed, which grow at the expense of the old ones. Annealing gradually destroys the texture; the new crystals are arranged disorderly. As the temperature is raised (or the metal is held longer at the annealing temperature), new grains grow and the old ones disappear. The grains can grow to such a size that they become visible to the naked eye. Annealing drastically alters the properties of a metal. It becomes more ductile and softer. This occurs because the grains become coarser and the texture disappears.

Chapter Three

Elements of Order in Disorder

1. Short-Range Order. Liquids

In the preceding chapter we found that many solids can be represented as close packing of spheres. The amount of free space in closest packing arrangements is about 26 per cent.

Among crystals with such a structure are, for instance, those of copper. Let us melt a piece of copper. What is the structure of the molten metal like? Experiments show that the volume of the substance increases by about 3% in melting. This is due to the increase in free space, which now equals 29% instead of 26%. The spheres have a free space at their disposal; they can leave their "proper" positions, disarranging the perfect order found in crystals.

To get a clearer idea of the mutual arrangement of the atoms in molten copper, we can resort to a plane model. Let us arrange a large number of billiard balls, packing them as close as possible in a limiting polygon. Then let us increase the area of the polygon so that the density (i. e. the number of balls per unit area) decreases in the same proportion as in melting.

Making use of some simple mechanical device, we next shake our model gently. The balls begin to jiggle about their equilibrium positions, surrounded by the same neighbours. Occasionally, when, by chance, an empty space of sufficient size is formed near a ball, the ball may slip in and change its neighbours.

Consider attentively the pattern of the arrangement of the balls. Can this arrangement be called complete disorder?

If we have microscopic disorder in mind, the answer will doubtlessly be in the affirmative, because we would have to specify the coordinates of all the atoms to describe the structure. But we shall not find here the macroscopic disorder that exists in gases. Let us ask ourselves: will any different distances between the billiard balls be equally justified? This is not entirely true for liquids.

As a matter of fact, no ball can approach any given ball so close that the distance between their centres is less than the

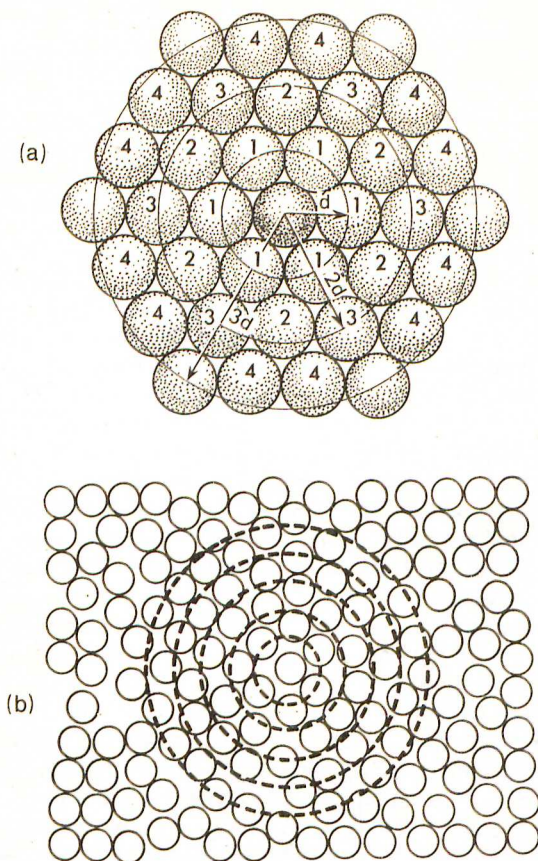


Fig. 27. (a) Ideal closest packing. Short-range order is perfect here: the centres of the billiard balls are located only on definite circles. (b) "Liquid" packing of balls. For the sake of clarity, the degree of loosening has been shown greater than the actually existing one.

diameter of the balls. This deviation from perfect disorder is also true for gases, but there it is of little significance because the distances between the nearest molecules of a gas are, on an average, ten times greater than the size of the molecules. Hence, notwithstanding the finite size of the molecules, we can speak of complete disorder with respect to a gas.

In order to demonstrate that the difference in the densities of gases and liquids is one of principle, a qualitative difference,

we should examine the neighbours of a given molecule, counting the molecules that are at a distance of one unit of length, two units of length, etc. from the given molecule.

This problem can be solved with sufficient accuracy but it will be clearer if we depict the molecules in the drawing as small circles on a plane. Next we centre our attention on one of the small circles and describe concentric circles about it with radii equal to two, three, four, etc. radii of the small circles representing molecules (Fig. 27).

Now we can answer the question: what is the average number of the nearest neighbours of the molecule being considered? By nearest neighbours we mean the molecules whose centres are in the nearest region that we have bounded.

The volume of the nearest region being known, as well as the number of molecules per unit volume (i. e. the density), we can easily find the data for liquids. The volume at the disposal of each atom of molten copper is only 3% larger than its own volume. Calculations show that there is an average of 11.6 atoms in the volume of the nearest region. Thus, there are about 12 nearest neighbours whose centres are at distances of its diameter from the given atom. There are no nearer neighbours.

Gases are an entirely different matter. In a gas, the volume of the nearest region contains, on an average, only 0.026 molecule. This means that molecules of a gas are in contact only in 26 cases out of a thousand. Owing to their finite volume, molecules cannot be closer together than when they are in contact. The jump from 0.026 to zero is not sensed by experiment. But the jump observed in liquids from 12 to zero (instead of from 0.026 to zero) is an abrupt one and is revealed by experiment.

This abrupt jump, however, is not the only difference between a liquid and a gas. The presence of a certain degree of order in the arrangement of the atoms of molten copper leads to other results as well.

Certain interatomic distances acquire more significance, standing out among the others. This is another basic difference between a liquid and a gas.

What interatomic distances are those most frequently found? They are ones close to the distances between nearest neighbours in the closest packing of spheres.

Let us examine Fig. 27*a* carefully. With ideal order on a plane, each small circle (or billiard ball) has six nearest neighbours at distances equal to their diameter. These are indicated in the drawing by the number 1. The next nearest balls also total

six (2); after which we have balls 3, also six, then balls 4, totalling twelve, etc.

In the case of "liquid" packing, each ball has somewhat more volume at its disposal, as we mentioned above. If ideal, or perfect, order could be retained in this increased volume, the number of nearest neighbours would be as before and the distances between the balls would increase by about one per cent. The difference is very small.

Let us now describe circles of the same diameters on the model of a liquid (Fig. 27b). Then we shall see that there are six balls whose centres are close to the first inner circle described with a dash line. As we depart farther and farther away from the central ball, the disordered arrangement becomes more and more evident for each successive sphere (they are called coordination spheres). Nearest-neighbour order gradually disappears and is continuously transforming into disorder.

This unique order with respect to nearest neighbours, which becomes less and less distinct as we move away from the atom or molecule being considered, is called short-range order. By short-range order we mean, of course, order in the macroscopic sense.

A feature of the structure of a liquid is that short-range order is the same for any atom. Only short-range order in the arrangement of their atoms is the same for both liquids and solids.

In discussing crystal structure, we found that atoms do not, by far, behave as spheres in all cases. This also affects the structure of liquids.

In the ideal case of short-range order in an atomic liquid, the nearest neighbours should number about twelve. What do experiments show? Metals, whose crystal structure can be represented by the closest packing of spheres, retain the same short-range order after they are melted: the average number of nearest neighbours is very near to twelve.

Each atom of lithium, sodium and potassium in a crystal has eight nearest neighbours as mentioned above. This same short-range order is retained in the molten metal, but still the average number of nearest neighbours becomes somewhat greater than eight.

Those simple substances in which the atoms are strongly bonded in the crystalline state to a small number of neighbours behave differently. When the substances are melted, these bonds are broken and the number of nearest neighbours of each atom in the liquid becomes greater than in the crystal.

2. Amorphous Bodies

The word amorphous, from the Greek *amorphos*, means without form. Amorphous solids are set off against crystals, which have the shape of a regular polyhedron. But a piece of metal need not have a regular shape, though it is certainly not amorphous. As we mentioned previously, most solids consist of tiny crystalline grains. In such bodies, their crystallinity is not necessarily manifested in their external shape.

What then is the basic feature of crystals and finely crystalline bodies? Primarily, this feature is a sharply defined melting point. If a crystalline body is heated, its temperature increases until it begins to melt. After that, the temperature ceases to increase, and the whole melting process proceeds at a strictly definite, constant temperature, called the melting point.

One of the specimens of amorphous solids usually cited is common glass. If we heat glass it gets softer and softer and is gradually transformed into the liquid state in a continuous process. If we put a piece of glass in a crucible and begin heating it, the following occurs. Almost imperceptibly the glass begins to melt down and spread until it finally assumes the shape of the crucible. A very thick viscous liquid is formed which, upon further heating, becomes less and less viscous and, at high temperatures, can be poured as easily from one vessel into another as water.

The behaviour of amorphous bodies can be explained by the special features of their structure which make us classify them as liquids rather than solids.

As we found in the preceding chapter, crystalline bodies have long-range order in the arrangement of their particles. Amorphous bodies have only short-range order in their particle arrangement and, in this respect, do not differ from liquids.

Schematic representations of the structure of quartz (silicon dioxide) and of quartz glass are illustrated in Fig. 28. They are chemically the same substance, which can be obtained in either the crystalline or the amorphous form. The resemblance and difference of these two states of the substance are quite evident from the drawings. We see that an amorphous body is a "spoiled" crystal. Both in crystalline and in amorphous bodies the number of nearest neighbours and the way they surround the molecule being considered are the same.

The lack in amorphous solids of long-range order, a typical feature of crystalline bodies, is directly responsible for the absence of a defined melting point. At the melting point in crystalline

bodies, a transformation occurs as a result of which long-range order disappears and only short-range order remains in the arrangement of the atoms.

As the temperature of amorphous bodies is raised, the type of arrangement of the atoms is not altered. Only their mobility is changed; their oscillations increase. First very few, then more and more atoms become capable of slipping out of their surroundings and changing their neighbours. Finally, the number of such changes per second becomes as large as for water.

Amorphous solids should be regarded as deviations from the normal state of affairs. Further on it will be shown that the crystalline state is natural for matter at a low temperature. But the formation of long-range order is not always a simple matter. The molecules of a substance may be of a shape that is inconvenient for regular and sufficiently close packing. Imagine, for instance, a spherical molecule with a long tail. Attempts to pack such figures closely and regularly will not be successful, while packing without long-range order may lead to a denser structure because parts of a molecule may bend, changing its shape. If various molecules are deformed differently, long-range order becomes impossible, but a close packing arrangement becomes quite feasible.

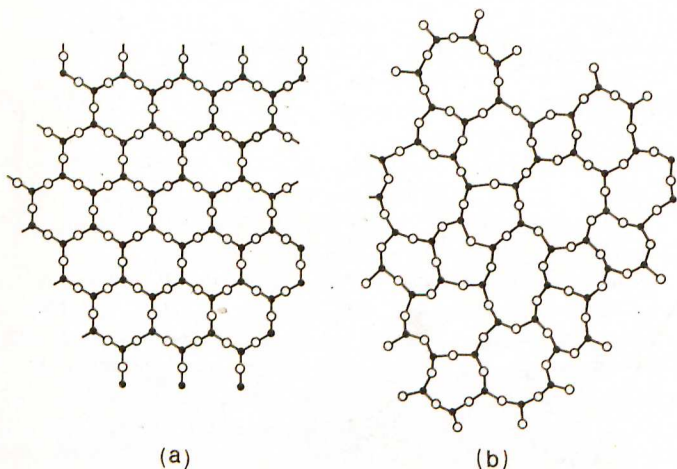
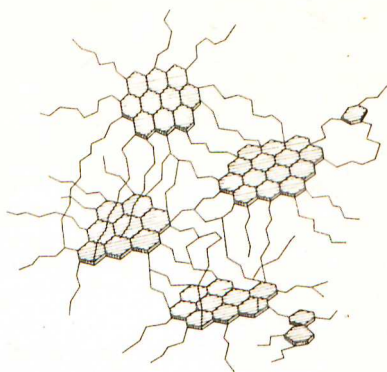


Fig. 28. Structure of quartz (shown schematically). Black circles are silicon atoms; white circles, oxygen atoms. The drawing simplifies the actual picture since it shows a flat model. From the standpoint of the illustrated model, amorphous quartz (b) has the "spoiled" lattice of crystalline quartz (a).

Fig. 29. Structure of the organic component of coal (shown schematically). The graphite networks are joined together by carbon chains. Sometimes, two or three networks may be pressed tightly together.



The author has established for organic molecules that however they are packed by nature into a crystal, not more than 40 per cent of "empty" space is formed.

If the shape of the molecules is such that the formation of long-range order leads to a larger percentage of empty space than the absence of such an order in a close packing arrangement, then no crystal is obtained. Such substances do not crystallize; they slowly thicken and become amorphous substances.

The particles of which a body is built up may be atoms, ions, radical-ions and molecules. It is obvious that in the last case the degree of order is higher, in a certain sense, because a molecule is a system of "rigidly" attached atoms, and since all molecules are identical, certain distances, namely, the intramolecular distances between the corresponding atoms in a molecular liquid (or amorphous body) are especially frequently found.

If the molecule itself has elements of periodicity, short-range order will be even more clearly defined. Such is the case in amorphous coal, in which a considerable share of the atoms form plane periodic networks. The larger the size of these networks and the greater the number of parallel networks, the higher the degree of order in the arrangement of the atoms of amorphous coal. A model of the structure of the organic component of coal is illustrated in Fig. 29.

Amorphous bodies also include a great many organic substances built up of giant molecules (consisting of thousands of atoms). Examples, are many plastics and plexiglasses.

The family of substances built of giant molecules deserves special attention and is to be discussed later.

3. Liquid Crystals

There are such substances as liquid crystals.

In other words, a "liquid crystal" is a "liquid solid body". Such a name is the same as saying: "sweet bitterness" or "quiet uproar".

What kind of bodies have got such contradictory names? We shall not introduce them by their complex chemical names, which would mean little to the reader. It is sufficient to note that this class of substances is quite extensive. Representatives of liquid crystals can be found among organic and bio-organic substances. The molecules of substances that form liquid crystals are always of elongated (rod) shape. Liquid crystals are found among viruses; they are also produced by lipoids, substances contained in living tissues.

The substance forming liquid crystals exists in this form in a definite temperature range. When a liquid crystal is heated, it turns into a liquid; when cooled, it becomes a crystal.

These substances have been thus named because they combine the properties of liquids and crystals in a remarkable fashion. They possess fluidity and form drops. But the drops are of elongated shape rather than spherical. Each drop resembles a piece of jelly. Detailed investigations show that the arrangement of the molecules in a drop has an order not found in ordinary liquids.

Two main types of liquid crystals have been discovered. The first has short-range order in the arrangement of its molecules, but all the molecules are parallel to one another. The order

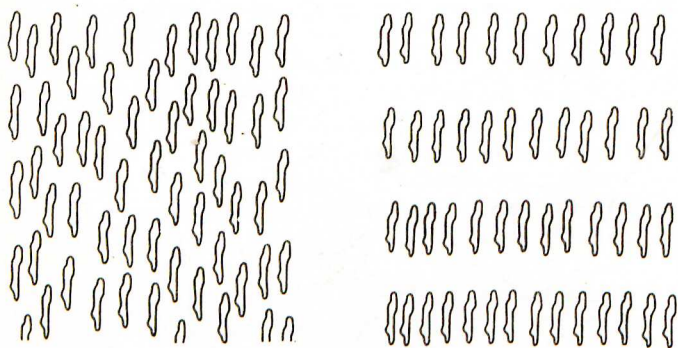


Fig. 30. Schematic diagrams illustrating the different kinds of arrangements of molecules in liquid crystals.

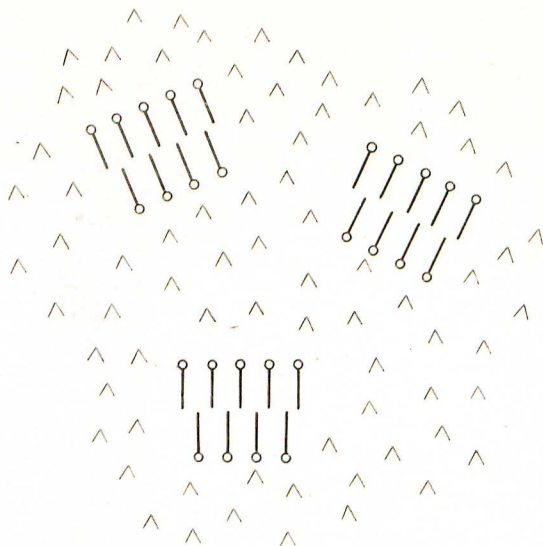


Fig. 31. Schematic diagram showing the arrangement of the soap molecules in a solution. With respect to the surface of the water, the soap molecules are on end. The small circles represent the polar ends of the soap molecules.

of molecular arrangement is even more strange in the other type of liquid crystals. The molecules are arranged in layers. Each layer consists of parallel molecules in short-range order with respect to one another. The two types are illustrated schematically in Fig. 30.

As a matter of fact, it would be difficult to find a better name for such substances than liquid crystals. The order of arrangement in them is more perfect than in ordinary liquids, but less regular than in crystals.

Soap forms liquid crystals when it is dissolved in water. The properties of soap that make it a cleansing substance are associated with its capacity to form liquid crystals.

According to up-to-date research, the structure of a soap solution is the following. The soap molecules are rod-shaped (about 4 angstroms across and 30 to 40 angstroms long). A negative electric charge is concentrated at one end. This polar end is attracted to the water molecules.

A soap solution is a liquid crystal consisting of a great number of double layers of soap molecules separated by layers of water

(Fig. 31). Each such double layer is oriented at random in the mass of water, but the polar ends of the molecules are always pointing outward, toward the water. The soap molecules within the layer are crowded but have short-range order. When there is not much soap in the water, the double layers of soap molecules are separated by thick layers of water. If we continue to dissolve soap in the water, we produce more and more double layers. The solution is saturated when the water layer is thinned down to about 20 angstroms.

The double layers forming the liquid crystal have high mobility. When we wash our hands, the layers slide easily with respect to one another and along our skin. The polar ends of the molecules pick up the dirt from the hands and yield it up to the water.

4. Thermal Motion in Liquids

We have already mentioned in passing that the molecules of a liquid are mainly engaged in thermal motions. In contrast to crystals, the equilibrium positions about which the molecules oscillate are not strictly fixed with respect to one another. Such motion would better be called marking time rather than oscillation.

Such "oscillation" of a molecule in a liquid takes place within the scanty volume available to the molecule. During this motion, the molecule remains surrounded by the same neighbours. After dozens or even hundreds of oscillations, one of the neighbours of a given molecule may, by chance, cease to be its nearest neighbour. Then it continues to "mark time" in renewed surroundings.

The ease with which a given molecule can change its neighbours is related to an important property of liquids: their viscosity. The less frequent the change of neighbours in a liquid, the thicker — more viscous — it is.

An increase in temperature, widening the amplitude of oscillation of the molecules, leads, naturally, to a reduction in viscosity. It should also be quite clear that, at the same temperature conditions, the more viscous liquid is one having molecules of complex, intricate shapes.

Many liquids solidify even before their viscosity increases to a considerable value. The high viscosity of glue, honey, fluid resin and heavy oil is due to the complicated shapes of their molecules.

Molecule interchange practically ceases when a viscous liquid solidifies. Kneading a piece of wood resin with our fingers, we

use external force to make the molecules of the piece change places. This, precisely, is what happens in so-called plastic deformation. Therefore, we can deduct that thermal motions of molecules also cause their infrequent and slow interchange in a piece of resin.

Only a heated piece of glass lends itself to plastic deformation. At room temperatures, glass can only be shattered. This means that, in solid glass, even thermal motion is unable to make the atoms change places.*

Now we can settle the dispute on whether glass belongs to the solid or liquid bodies. Evidently, such amorphous bodies as glass have features of both solids and liquids. The type of mutual arrangement of the atoms in glass is the same as in a liquid: the arrangement has only short-range order. On the other hand, the kind of motion of the atoms in an amorphous solid is typical of crystals in that an atom in motion maintains its unaltered surroundings: its neighbours do not change places.

5. Types of Order Put in Order

We began our discussion of order by asking the reader not to confuse macrodisorder with microdisorder. We should recall that a rigorous definition of these concepts is closely associated with the amount of information we must specify to arrange integers in a certain series. But the same is true for arranging various figures, atoms or molecules in a definite sequence. It makes no difference, here, whether we are dealing with linear or three-dimensional order.

We have also considered the problem of short- and long-range order. What relation do these two terms have to our division of order into micro-order and macro-order? The answer is that there are different ways of dividing something according to different features. It is the same, we may say, as the division of pieces of meat according to their weight and according to their fat content. Division into micro- and macro-order and division into short- and long-range order are classifications according to different qualities.

Does this mean that there can be a system of particles in which we find microscopic short-range order, microscopic long-

* It would be more correct to contend that such interchange is very rare. It takes place in crystals as well, chiefly because of their imperfection.

range order, macroscopic short-range order and macroscopic long-range order? The question is properly put. That, exactly, is the case.

Imagine, for example, very carefully stacked sacks of potatoes. The centres of the sacks form a regular three-dimensional lattice. But inside each sack we have complete disorder. How do we classify such a system? It has macroscopic long-range order, but has no microscopic order. The system, however, has both long- and short-range macroscopic orders.

You want to get rid of long-range order? We meet no difficulty in conceiving of such a system. It is sufficient to assume that the sacks have been heaped at random. But this "at random" is also relative. We know now that each sack will have an average of twelve nearest neighbours. Hence, we rid ourselves of long-range order, but short-range order remains.

Now for another example. Imagine a system of symmetrical polyatomic molecules. The molecules are identical and the atoms that form them are arranged at exactly the same distances. Lines connecting the atoms make identical angles with one another. Hence, such a system has microscopic order. But the molecules themselves can be differently arranged. They can be in disorder; they can have distinct ideal long-range order, when the molecules form a perfect crystal; or the molecules can closely adjoin one another so that we have macroscopic short-range order.

It proves expedient to properly classify each case of order that we may deal with. The preceding discussion is sufficient, we feel, for the reader to realize that the division of order into short- and long-range orders and the division of order into the macroscopic and microscopic varieties can be combined in any manner and that all these combinations are actually found in the world of molecules and crystals.

Such combinations are of especial interest when we are dealing with the world of living tissues. We find tissues in which there is no microscopic order, only long-range macroscopic order. Such is the case with the structure of muscles, which consist of actin and myosin; such is the case with crystals and molecules of DNA (deoxyribonucleic acid).

You will also find some examples in this book.

Elements of Disorder in Order

1. Thermal Motion in Crystals

We have already become acquainted with the representatives of order in the world of atoms. Crystals are bodies with the most regular structure. We described the structure of a crystal as mathematically ideal straight lines along which atomic arrangements are repeated at strictly identical distances.

We embellished the truth to some extent, however, in describing crystal structure. A real crystal is much more complex than the ideal "three-dimensional wallpaper" we used to demonstrate its structure. In the first place, we should recall that the motions of the particles of a crystal about their equilibrium positions are complex and diversified.

If we could take a high-speed still photograph of the arrangement of particles in a crystal, we would see that it does not have truly regular lattice structure. Thermal motion, without which no form of matter is conceivable, is manifested as continuous vibrations of atoms, ions and molecules. The space lattice we discussed previously is formed by particles in their mean — equilibrium — positions. The amplitude of thermal vibrations is fairly large, and increases with the temperature. At room temperature, it reaches 0.1 or 0.2 angstrom, which may amount to several per cent of the spacing (called the lattice constant) after which the crystal structure is repeated. At any given instant, a part of the atoms are passing through their mean positions, a part are in their extreme positions and the rest are in some intermediate position. This is why a high-speed still photograph cannot show a regular space lattice.

Depending upon the kind of forces binding the atoms, the particles of a crystal may have different types of vibration with different amplitudes. If the crystal is made up of molecules instead of atoms, the most distinct motion is that of the molecules as whole units. Molecules make both straight-line and torsional vibrations.

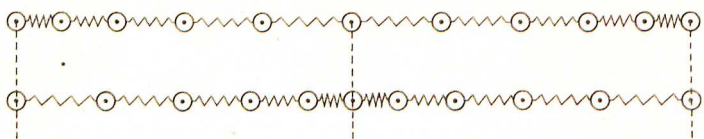


Fig. 32. Balls joined together by springs behave just like the atoms of a single row of crystal lattice points. The atoms are bonded by forces of electric origin. These forces can be conditionally conceived of as little springs. The drawing shows the positions of the balls at two different instants. In one, the three middle balls are stretched apart to their limiting positions; in the other, they are compressed to their other limiting positions.

The vibrations of particles in a crystal are ordered to a certain degree. This is due to the bonds between the particles. Imagine a row of identical balls joined together by identical springs (Fig. 32). If one ball is pulled or pushed out of its equilibrium position it will pull along a second ball, and then a third, etc. This creates a sort of wave, rolling along the whole row of balls. The same occurs in a crystal: the vibrations of the various particles are not independent of one another. The deviation of particles from their equilibrium positions is associated with the deviations of neighbouring particles from equilibrium positions.

2. Gaseous Crystalline State of Matter

Did you ever hold a piece of camphor in your hand? This is a solid substance, but when we employ the word "solid" we cannot help but feel that our language is sometimes inadequate. Of course, a piece of camphor is not a liquid, but it is so easily crushed by your fingers.

There are an immense number of such weakly cemented solid substances. Almost all of them belong to organic substances, and their characteristic features are evident, not only to the touch, but in appearance as well: a cloudy, shapeless blob of matter. Maybe they are some kind of unique amorphous glass? No, these substances belong to a highly interesting class of solids for which we shall have to suggest another name.

The basic feature of camphor-like substances is that their component molecules form a quite regular lattice only with respect to their centres. As to the orientation of the molecules, it may be any random one, as in a gas. Imagine a formation of soldiers in a rank on parade after the command "Attention!"

has been given. This formation can be compared to a crystal: strictly regular arrangement of the centres of the bodies and their strictly ordered orientation (all bodies are turned in exactly the same direction). If we now give the command "At ease!" the soldiers maintain their positions, but can turn their bodies at will. The centres of the bodies continue to form a regular lattice, but the orientation of the bodies is disordered.

Disordered orientation of the molecules can be explained by the fact that they are continuously rotating or that they occupy a position in the lattice at random, "congealed" angles of rotation. Which of these two possibilities has nature given preference to in the given case? A comprehensive study of the properties of such substances has shown that the first explanation is correct.

It became necessary to give a special name to a state of matter with such a unique combination of order and disorder. We have the choice of two terms that have been suggested: the rotational crystalline state and the gaseous crystalline state. The latter emphasizes the combination in a single substance of the special features of crystals and the characteristics of gases.

The rotational crystalline state did not attract any particular attention for a long time. "Rotational freedom" was regarded as a rare case of anomalous behaviour of molecules in a crystal lattice. Today, this viewpoint has been abandoned. A fairly large number of such substances have already been investigated, and certain general laws pertaining to their structure have been discovered. It turned out that the gaseous crystalline state of matter is developed when, in their rotation, the molecules do not push apart their neighbours very vigorously and, therefore, violate close packing only slightly.

In other words, the shape of the molecules should resemble a sphere or cylinder. In the first case, the centres of the molecules are arranged in long-range order; and in the second, their axes. Spherical molecules in the rotational crystalline state form one of the closest packing arrangements for spheres having either cubic or hexagonal symmetry of their crystal lattices. Such packing is typical, for instance, of camphor molecules. The shape of many chain molecules is almost cylindrical. In such substances, a structure with rotating molecules is an arrangement with close-packed cylinders, like the one that can easily be obtained with a handful of pencils tightly clutched. This structure is found in various paraffins and many other substances.

Such substances are usually oily to the touch, slightly resemble wax, but are transparent. A typical feature is their low hardness;

faceted shapes are difficult to form of such materials. This state exists in a definite temperature range, which is always just below the melting point. This can readily be understood: the transition from the crystalline state to the rotational crystalline state is the first stage in melting. The partial loss of long-range microscopic order can be called "orientational melting".

The melting process in gaseous crystalline substances proceeds as if it were divided into two steps: first the orientation of the molecules "melts", and then long-range order "melts" in the arrangement of the centres of the molecules.

There are forces of interaction between atoms of matter: more distant atoms attract each other, closer atoms repulse each other. This means that there must be distances at which these forces balance each other. These are the equilibrium distances at which the particles tend to be with respect to one another. In particular, this leads to the formation of long-range order in crystals. Hence, the first factor is the tendency to order. At the same time, the greater the order in the arrangement of the particles of a substance, the less the freedom for their thermal motion. When the temperature is raised, the necessity arises for more freedom in the motion of the particles. But thermal motion tends to arrange the particles in complete disorder. Hence, the second factor is the tendency to disorder.

When the thermal oscillations are sufficiently small (at a low temperature), the tendency to order prevails. Under these conditions, a crystalline solid is more stable. As the temperature is raised, the tendency to order in crystals is not appeased. Then the substance melts or even evaporates. From this point of view, the liquid crystalline and rotational crystalline states are to be regarded as attempts of nature to "reconcile rival factions" to some extent.

In the rotational crystalline state, the rounded shape of the molecules enables a structure to be formed in which the tendency to order is complied with by the existence of a crystal lattice of the centres of the molecules, and the tendency to disorder, by the rotation of the molecules.

As the temperature is lowered, the molecules begin, sooner or later, to "straighten out" their orientation, order prevails over disorder and the gaseous crystalline state is converted, with an abrupt change and at a definite temperature, into an ordinary crystalline substance.

Methane, the main part of city gas, freezes at a temperature of 182°C below zero. Here, the gaseous crystalline state is

formed; it is converted into the crystalline state only after a further drop of 71 deg C, i.e. at a temperature of 253°C below zero.

Thus, thermal motion can spoil the order in a crystal to the extent that crystallinity remains only with respect to the centres of the molecules. What a vital element of disorder in order!

3. Block Structure

Experiments have shown that each crystal consists of separate blocks turned slightly with respect to one another (Fig. 33). Let us pull a straight thread through the centres of a row of atoms. The first, second, third, ... and hundredth atom are strung on the still straight thread. But beginning with the 101th or perhaps the 501th atom, the row begins to deviate from the line of the straight thread, making a small angle (from half a minute to dozens of minutes of arc). If we want the thread to run

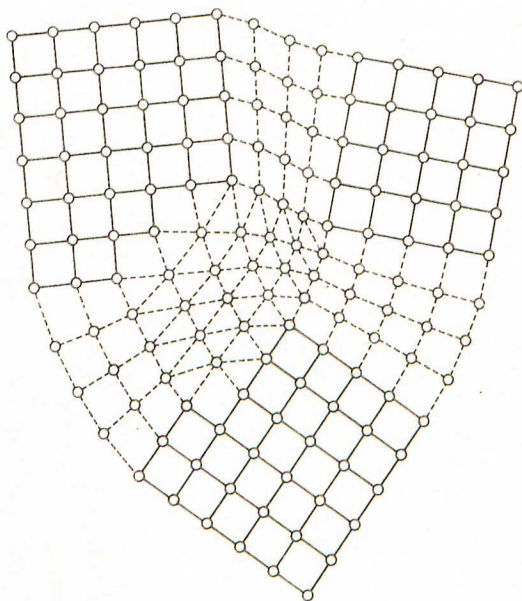


Fig. 33. Schematic illustration of block structure in a crystal. For the sake of clarity, the angles through which the blocks are turned with respect to one another have been drastically exaggerated.

along the row of atoms, we will have to bend it slightly at some point. This will be followed by another straight portion, until at some point a new slight turn is required. The points at which the thread has to be bent coincide with the boundaries of the block. Each block is a piece of perfect structure (so we shall call it for the time being). Bends in the thread are both to the right and to the left. Therefore, on an average, the general direction of the row of atoms through which we strung the thread is maintained with great accuracy throughout the whole crystal.

Block structure is due, evidently, to the difficulty of maintaining ideal long-range order over a great distance. This difficulty is similar to that experienced in trying to build a high tower of toy blocks. You carefully place each successive block, but, beginning with some story, say the tenth, the stack becomes unstable.

Block structure of crystals indicates that ideal order is violated.

4. Dislocations

Not so long ago, William Lawrence Bragg, who has played an exceptionally significant role in the investigation of crystal structure, proposed a method of simulating the arrangement of atoms in crystals by means of soap bubbles. A photograph of the surface of a liquid (Fig. 34) covered with tiny soap bubbles excellently demonstrates many features of crystal structure that we now intend to discuss.

In the photograph we see two differently oriented "crystalline grains". The boundary between them is of irregular structure. It has many vacancies and the atoms in this transition region are not closely arranged. The presence of vacancies indicates that foreign impurities are most probably located precisely in these transition regions as has been mentioned previously.

The most interesting feature of this model, however, is not the boundary between the two grains, but that between two blocks of the same grain (at the right in the photograph).

This boundary is shown in the illustration by an arrow. Now if you carefully examine the bubbles, you see that the row of bubbles slightly changes its direction as they pass over the boundary. As you glance along the boundary of the blocks, you find one severely spoiled spot. Look carefully, the cause of the violation in order is that the number of horizontal rows to the right of the boundary is one less than the number of horizontal

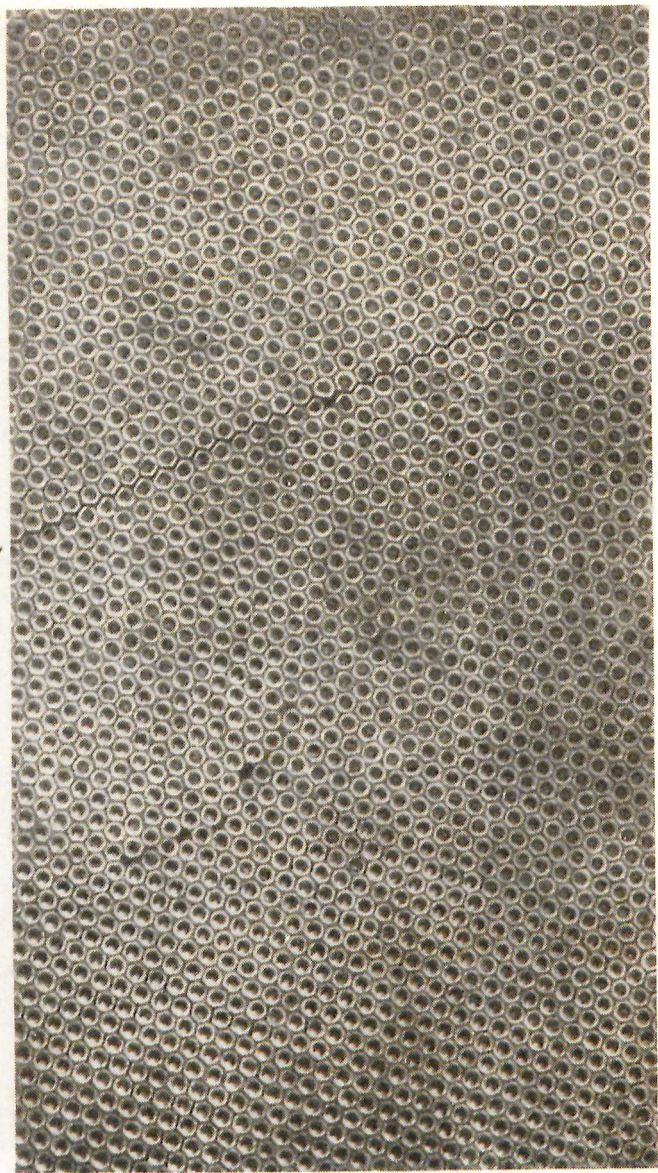


Fig. 34. The surface of a liquid covered with soap bubbles. There is a far-reaching analogy between the arrangement of soap bubbles and that of the atoms in a crystalline solid.

rows to the left of the boundary. In other words, an extra row has "sneaked" into the left block.

The photograph shows a two-dimensional model of a crystal. A little imagination and you can visualize a picture of a crystal spoiled in a similar manner. Each row of circular bubbles can be regarded as a projection of an atomic layer perpendicular to the photograph.

The severely spoiled spot, seen in the photograph, corresponds, in a three-dimensional crystal, to a linear region perpendicular to the plane of the illustration. Such a place is called a dislocation, in the sense that it is a disarrangement or displacement. The presence of dislocations is the cause (or, in any case, one of the causes) of the block structure of crystals.

As will be seen further on, the idea of dislocations explains many other phenomena besides the block structure of crystals. We can profit, therefore, by studying these peculiar distortions of crystals in more detail.

There are two general types of dislocations: linear and screw dislocations. The linear type is the one we found in the bubble model. A linear dislocation is illustrated schematically in Fig. 35 *a*, where it is denoted by the overturned letter T. To "see" a dislocation we must examine the boundary between two blocks (shown by a dash line). The layer of atoms above the boundary contains one row of atoms more than the adjacent layer below the boundary. The region of the dislocation is located close to a line passing along the boundary. Here we have maximum distortion of the crystal lattice; it rapidly dissipates to either side of the dislocation line. The same illustration shows a top view (Fig. 35 *b*) of two atomic planes, adjoining the block boundary on two sides. The upper (compressed) plane, shown with full lines, has one row more than the lower plane (dash lines).

Analogous schematic diagrams of a so-called screw dislocation are shown in Fig. 36. Here the lattice is divided into two blocks, one of which has slipped, as it seems, by one lattice constant with respect to the other. Maximum distortion is concentrated at the axis shown in the diagram. The region adjoining this axis is what is called a screw dislocation.

We shall understand the nature of this distortion better if we look at the other diagram (Fig. 36 *b*), which illustrates two adjacent atomic planes on the two sides of a vertical plane passing through the axis (the one along which slip has occurred). With respect to the three-dimensional view, this is a projection showing the planes from the right. Here we see the axis of the

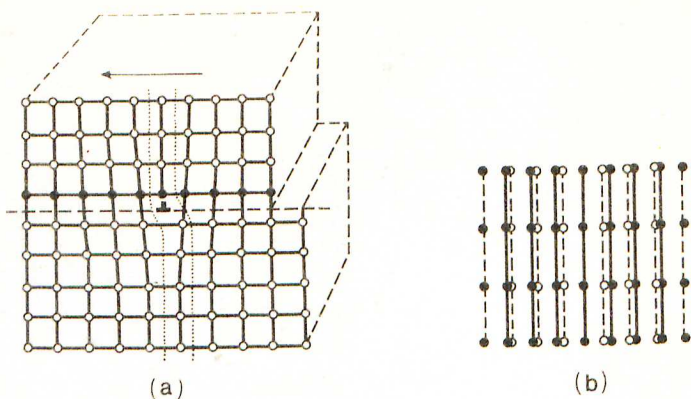


Fig. 35. (a) Schematic diagram of a linear dislocation. The layer above the dash-line boundary has one row of atoms more than the layer below the boundary. (b) Layers of atoms above (full lines) and under (dash lines) the boundary between blocks. This picture is very schematic. Close to truth is Fig. 34. Compare it carefully with this drawing.

screw dislocation, the same as in the other drawing. The atomic plane belonging to the right-hand block is shown by full lines, that belonging to the left-hand block, by dash lines. It is evident from the drawing that a screw dislocation is another type of distortion, differing from that of a linear dislocation. There is no extra row of atoms. The essence of the distortion

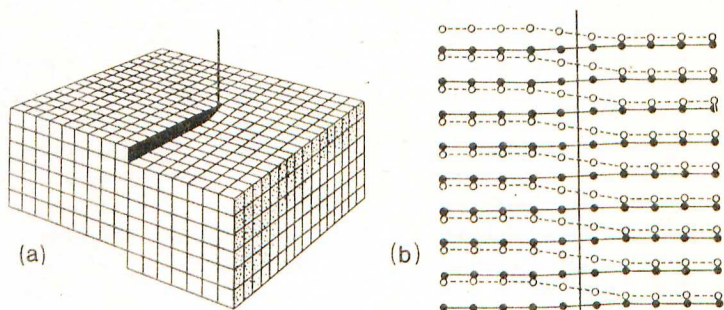


Fig. 36. (a) Schematic diagram of a screw dislocation. (b) Cross section of (a) showing two atomic planes adjacent on both sides to the plane of the section; the black circles are located closer to the reader than the white circles.

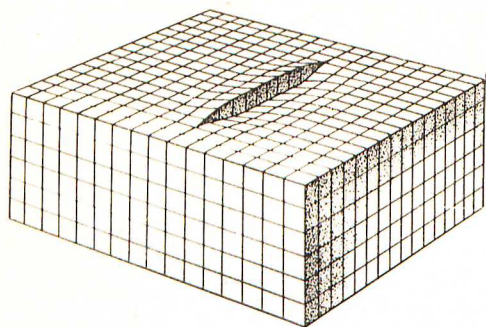


Fig. 37. Distortion produced by an array of two successive screw dislocations with opposite hands of rotation.

is that the rows of atoms change their nearest neighbours near the dislocation axis. They bend downward to align themselves with the neighbours located one story below.

Why is this called a screw dislocation? Imagine yourself strolling along the atoms (after reducing your size to subatomic dimensions) having decided to pass around the dislocation axis. It is obvious that if you start your journey on the lowest plane you will find yourself one story higher after each turn. Finally, you will emerge on the top surface of the crystal, as if you had been climbing winding stairs in a helix like the thread of a screw. In our drawing, the climb is in the counterclockwise direction. If the slip of the blocks has been in the opposite direction, your journey would have been clockwise.

Screw dislocations with the same hand of rotation may follow, one after another, in a single crystal. If, however, there are two dislocations with opposite hands of rotation in a single plane, the interesting distortion shown in Fig. 37 is formed.

5. Dislocations Travel

To see a dislocation in a crystal under a microscope and to watch its motion would be a difficult problem. Whether or not the guess about the existence of dislocations in crystals is correct is a matter in which we must base our judgement on the consequences that follow from the diagrams and models we have just discussed.

First of all, let us consider how deformation should occur in a crystal with and without dislocations. This is illustrated by the diagrams in Figs. 38 and 39.

Such shear requires great force

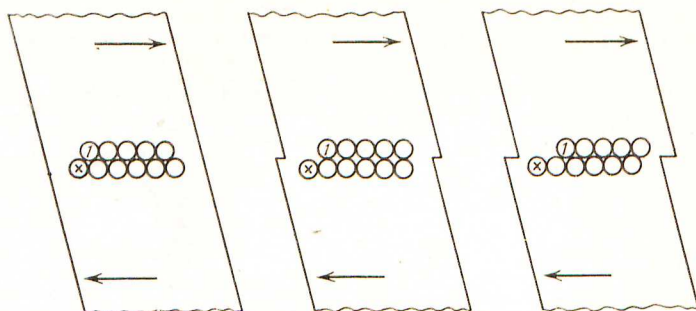


Fig. 38. This would be the mechanism of displacement of one atomic plane with respect to another (shear) if there were no dislocations. Shear proceeds gradually. The initial, intermediate and final positions are illustrated.

Such shear requires much less force

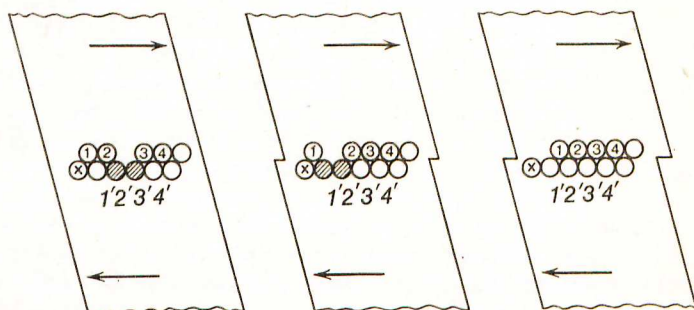


Fig. 39. Probable shear mechanism. Until the dislocation runs through the crystal, no shear occurs. At the final instant, shear occurs suddenly, in a jump. Shear is transmitted through the crystal like a compression pulse, from sphere to sphere.

Assume that we want to shift the upper half of the crystal with respect to the lower half by one interatomic distance. It is evident in Fig. 38 that we must roll all the rows of atoms in the shear plane over one another. The shear plane is the one along which displacement occurs. It is an entirely different matter when a shear force acts on a crystal containing dislocations.

Figure 39 illustrates a close packing arrangement of spheres (only the end spheres of the rows of atoms are shown) containing

a linear dislocation. For the sake of simplicity, we assume that the region of the dislocation extends over a minimum number of rows. We can say then that the dislocation consists in the following. Between two rows of the upper (stretched) plane adjoining the boundary, or interface, between the blocks, there is a linear void (something like a fissure). As to the lower (compressed) plane, adjoining the block interface from the other side, it has an extra row of atoms.

When we introduce this extra row, the two rows of atoms directly under the "fissure" are excessively compressed so that the atoms lose their spherical shape.

We begin to shift the upper block to the right with respect to the lower one.

To help you understand what is happening, we have given numbers to the rows, with primed numbers for the spheres of the compressed layer. At some initial moment, the "fissure" is between rows 2 and 3; the compressed rows are 2' and 3'. As soon as the shifting force is exerted, row 2 moves into the fissure; now row 3' can "breathe freely", but row 1' will have to squeeze into less space. What has happened? The whole dislocation has moved to the left, and its motion continues in the same way until it "emerges" from the crystal. The result is a shift over one row of atoms, i.e. the same as in the shear of a perfect crystal shown in Fig. 38. In other words, shear consists in the motion of a dislocation line along the shear plane.

It is evidently unnecessary to prove that much less force is required in the second case. In the first case, we had to overcome the interaction between atoms in rolling over all the rows simultaneously. In the second, only a single row of atoms is involved at each instant.

Calculations indicate that the strength of crystals in shear, assuming there are no dislocations, should be a hundred times greater than that actually observed in experiments. The presence of even a slight number of dislocations can reduce the strength of the material by a substantial factor.

The preceding discussion poses a question that must be cleared up. It is evident from the drawing (Fig. 39) that the applied force "drives" the dislocation out of the crystal. This means that the crystal becomes stronger and stronger as we increase the degree of deformation. Finally, when the last dislocation is eliminated, the crystal should, according to the theory, become a hundred times stronger than a perfect, regular crystal. The crystal is actually strengthened in the course of deformation, but far from

a hundredfold. The screw dislocations save the day. It was established (and here the reader will just have to take our word for it because it is difficult to illustrate it with a drawing) that it is not so easy to drive the screw dislocations out of a crystal. Besides, shear of the crystal may take place with the aid of dislocations of both types. Dislocation theory is satisfactorily explained by the features of shear phenomena along crystal planes. According to up-to-date views, plastic deformation of crystals consists in the motion of disorder along the crystal.

Can we consider the block structure of crystals as being congealed if no forces are applied to them? The answer is no. The thermal motion of the atoms cannot but affect the dislocations. Thermal motion of dislocations along grain boundaries is feasible. Disorder prowls through the crystal and, evidently, can continuously change the configuration of the blocks, creating new boundaries and destroying the old boundaries between the blocks.

Much remains to be investigated by physicists before they are able to put together a distinct picture of this unceasing struggle between order and disorder that comprises an essential part of the "life" of a crystal.

6. A Perfect Crystal

Is it possible to obtain a perfect crystal and to check whether the strength of a dislocation-free crystal is actually about a hundred times that of an ordinary crystal? About 10 or 20 years ago such crystals were found accidentally. They were extremely thin (of a thickness less than a micron) threads of monocrystalline tin. They had grown very slowly under ideal conditions. Besides, their small size provided no room for dislocations. The strength of these monocrystals exceeded that of common large crystals by almost a hundredfold.

This discovery attracted so much interest that persistent efforts were made to find other perfect crystals. And they were found. It appears that thin perfect crystalline needles, called whiskers, can be obtained, if sufficient pains are taken, from many and, most probably, from all substances.

So far, nobody has been able to grow large defectless crystals. It may be that structural perfection is a property of only such threadlike formations. This is still an open question. It is only known that, in comparing crystalline threads of various thicknesses, the thinnest prove to be the strongest.

Many exceptionally interesting experiments can be performed

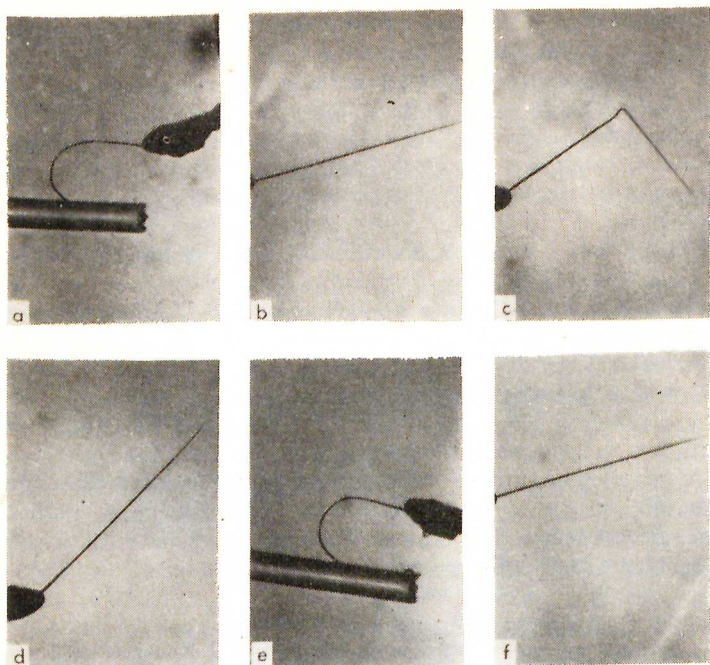


Fig. 40. Experiments with a threadlike crystal (whisker) of copper.

with threadlike crystals, but we shall consider only one, which illustrates the tendency of the threads to maintain their perfect order. Shown in Fig. 40a is a threadlike crystal of copper 2.5 microns thick which bends like a rapier. The next photograph (Fig. 40b) was taken to demonstrate its elasticity: the crystal straightened out when the load was removed. Then we decided to bend the crystal plastically (Fig. 40c): the load was removed and the crystal stayed bent. After this, the thermal motion of the atoms was facilitated by holding the bent thread for ten minutes at high temperature. Freedom of motion of the atoms turned out to be sufficient to restore the perfect lattice. The thread straightened out by itself (Fig. 40d), and all its elastic properties were restored as we can see from the last two photographs in which the first experiment was repeated with the restored crystal.

Thus, it appears that, under certain special conditions, we can drive almost all the elements of disorder out of a crystal.

7. Intrablock Defects

As we now know, a crystal lattice consists of blocks, with dislocations "strolling" along the block boundaries. How about inside the block; what lacks of perfect structure can we find there?

Here, too, we observe elements of disorder. The lattice may have defects in the form of voids (vacancies), as well as in the form of impurities consisting of foreign atoms. There may be a negligible number of vacancies and a small amount of impurities, but the distortion they cause is considerable. The nature of this distortion is illustrated by Fig. 41. The drawings show the

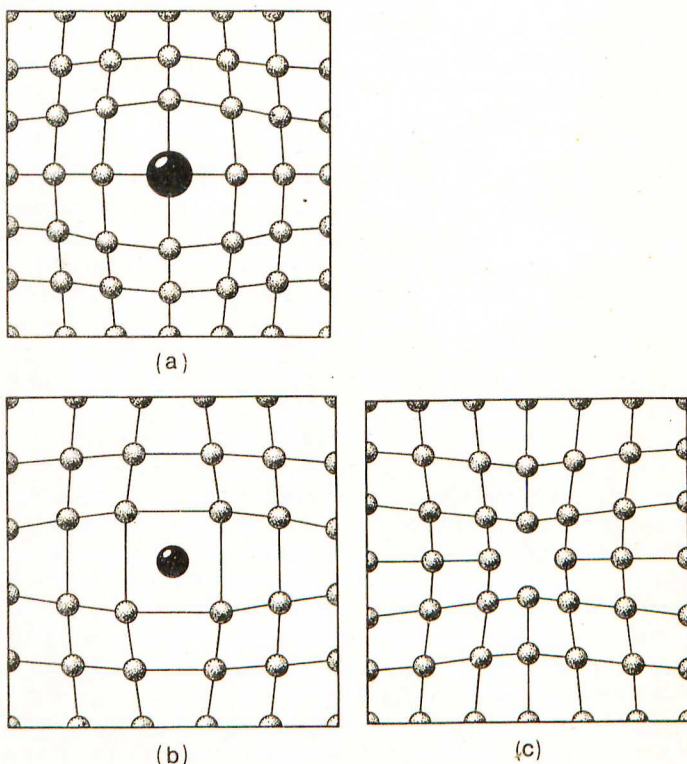


Fig. 41. Lattice distortion due to various causes. (a) This is what happens if a large impurity atom replaces a host atom. (b) Distortion caused by a foreign atom in an interstice. (c) Distortion of the lattice when an "atomic site" is vacant.

effects of a vacant lattice point (site) of an atom which has got between the atoms of the basic lattice, and of a foreign atom which substitutes for one of the atoms of the basic lattice.

The influence of such defects may extend in all directions within a sphere with a radius of 5 to 10 lattice constants. But 10 lattice constants in all directions means that as many as 1000 unit cells are affected. This is why an impurity whose content is of the order of 0.1% can fundamentally alter the properties of a crystalline substance. True, we must immediately make a reservation: the effects of impurities do not lead to appreciable distortion of the lattice.

One striking example is appropriate here. In a crystal of germanium (or silicon), each atom has four nearest neighbours. The bond between each pair of atoms is provided by a pair of electrons. Germanium has four valence electrons; this obligation lies on them.

Now imagine that an atom of germanium has been replaced by an atom of arsenic. The newcomer is obliged to obey the rules concerning bonds in germanium. The guest atom of arsenic gives up four of its valence electrons as bonds with the neighbouring host atoms of germanium. But arsenic has five valence electrons. One unsettled electron remains unemployed and acquires the capacity to rove about in the germanium crystal. Thus an addition of arsenic atoms imparts electronic conductivity to germanium. If voltage is applied to the crystal, these spare electrons begin to move in an ordered manner, i.e. they produce an electric current.

Assume now that a trivalent aluminium atom has replaced an atom of germanium. Naturally, it can only be bonded to three atoms of germanium. One bond is lacking, and a "hole" (a place lacking an electron) is formed. It is well known, however, from electrostatics that the place from which an electron has been removed behaves like a positive electric charge. That is how our "hole" behaves. If we apply voltage to a germanium crystal with an addition of aluminium, the holes begin to move in an orderly manner and electric current passes through the crystal. This is known as hole conductivity.

Imagine a row of men standing, one behind another, in strict order. One man steps out of line. To restore order, the next man steps forward into the place of the one who left the file, then the following man fills the new vacancy and so on down the file. But this motion can be described otherwise: the vacancy moves in the opposite direction. This is precisely

what happens in the motion of a "hole". When voltage is applied to the crystal, the adjacent electron "jumps" into the hole, then the next electron jumps into the new hole, etc. The "hole" has started to move.

If we have a crystal of germanium and have established by experiment that it has, say, electronic conductivity, we can reduce this electronic conductivity by adding atoms of aluminium to the crystal. This is called "doping". Finally, if we keep on adding aluminium, at some instant we transform it into a crystal with hole conductivity. It has been shown experimentally that the balance between the holes and free electrons can be disturbed by adding a single atom of impurity per thousand million atoms of germanium. It is clear, now, what a tremendous role is played by even an insignificant amount of impurities.

The production of germanium crystals of various types is of paramount importance in engineering. If one small crystal with hole conductivity is sandwiched tightly between two small crystals with electronic conductivity, or vice versa, we obtain a wonderful device, called a crystal, or semiconductor, triode. It has the same functions as a vacuum-tube triode but surpasses it in many respects.

A description of the application and principle of these triodes is beyond the scope of this book.

8. Crystals with Errors

The simplest close packing arrangements of atoms forming crystals are the hexagonal type, in which the third layer is directly above the first, and the closest cubic type, in which the fourth layer is above the first.

We mentioned previously that a countless number of different stacking arrangements are possible that differ from one another only in the sequence of their layers. If we look at a closest packing arrangement of spheres along a normal to the layers, we find that the layers can be classified into three types: A, B and C. All A layers have each atom in line, one above another. All B layers are arranged in the same manner, with each atom in line, one above another, and the atoms of the C layers are one above another. If we call the first layer A, then layer B has its spheres (or billiard balls) lying directly over the white hollows of layer A, and layer C has its spheres directly over the blacked-in hollows of layer A. There can be no other kinds of layers in closest packing (see Fig. 12).

Making use of this notation, we can readily describe various

closest packing arrangements by literal formulas. For example, hexagonal packing has the formula ...ABABAB..., and cubic packing, the formula ...ABCABCABC.

Any sequence of layers may be typical of ideal long-range order if, beginning with some layer, it repeats itself. For instance, the sequence

...ABABCACBCABABCACBCABABCACBC...

corresponds to a perfect crystal in which the sequence is repeated after nine layers.

Close packing arrangements are observed in nature that have no repetition in the sequence of their layers. Such "crystals" are an interesting example of a mixture of order and disorder. The arrangement of the atoms in each layer is completely ordered, but there is no order in the stacking of the layers. This is the case that we have already mentioned, in which we have order in two directions and a lack of order in the third.

The structure of these bodies, in which order is so interestingly combined with disorder, is worth more detailed discussion. Such packing is produced in nature with different degrees and kinds of orderliness.

Consider, for instance, a growing crystal in which the stacking of the layers complies with the hexagonal law:

...ABABABAB...

At some point an error occurs, and the ninth layer is stacked according to the cubic law:

...ABABABABC...

After this, the crystal continues to grow according to the hexagonal law:

...ABABABABCACACACACACACA...

until another "error" occurs:

...ABABABABCACACACACACACACAB...

with further "proper" growth:

...ABABABABCACACACACACACACABCBCBC...

A "crystal" is obtained with separate portions having correct structure. The errors create an element of disorder in the structure. If the frequency of such "errors" increases, we finally obtain a body ordered in two dimensions (ordered layers) and disordered in the third (disordered stacking of layers).

We cannot specify concisely with respect to the above-described system of atomic layers with stacking errors whether it is ordered or disordered. Order and disorder are combined and do not allow us to classify such a body as either a crystal or an amorphous solid.

An example of the bodies we have been discussing is cobalt. By prolonged high-temperature annealing of finely powdered cobalt we can grow quite large grains which consist of a system of close-packed layers. A grain consists of large portions in which the layers are packed according to the law ...ABCABC... (cubic phase) and small packets of 9 or 10 layers each of the ...ABAB... type, separated from one another by "cubic" errors. A series of such packets makes up what can be called the hexagonal phase of cobalt.

9. Order and Disorder in Binary Alloys

We should not presume that the letter arrangements we just dealt with are of purely academic interest. The structure of matter is closely related to its properties. Pure metals are much less employed in engineering practice than alloys. Binary alloys are most extensively applied in metallurgy. We shall discuss them in the following.

It was found that an approach from the viewpoint of close packing of spheres is applicable to binary alloys as well. Many alloys of two metals consist of a close-packed arrangement of spherical atoms. Close packing is feasible in two cases: when the atoms of the two metals are of approximately the same size, and when the atoms of one kind are quite large and those of the other kind are quite small.

In the second of these cases, the close packing of spheres, discussed above, comprises the large atoms. The small atoms occupy the voids (interstices) of the packing arrangement. These are called interstitial alloys. One of these, for instance, is the alloy of iron (large atoms) and carbon (small atoms), which we call steel.

The other cases, in which the atoms of the components of the alloy are of about the same size, are also sufficiently frequent. Alloys of copper and gold can be given as examples. If the addition of one element to another results in the substitution of the atoms of the added metal (also called guest atoms) for the atoms of the base metal (host atoms), i.e. spheres forming the close packing arrangement, the alloy is said to be substitutional. We shall give our attention to this type of alloy.

Imagine that such an alloy is built of atoms of a single kind. The model of alloy structure can be visualized as close-packed spheres (with layers stacked according to a hexagonal or cubic rule). A layer of "black" spheres is sandwiched between layers of "white" spheres.

If we have available a large number of white and black spheres, we can construct a great variety of close-packed arrangements. We assume, first, that we have an equal number of black and white spheres for building a two-coloured figure. This can be readily done as follows



i.e. we can arrange them in regular simple alternating layers of white and black spheres. With a little more imagination, we could come up with something like this:



i.e. alternate equal amounts of white and black spheres. Such atomic structures are actually observed in many alloys. The first is called a simple ordered structure and the second, a superstructure, or superlattice.

In some alloys, however, we find disordered stacking, for example:



or



Any order in the succession of the layers has disappeared; the layers are in disordered arrangement.

The complete disorder of the last but one picture is in the fact that of the 20 black layers 10 have white right-hand neighbouring layers, and about half (actually nine) have black ones. In exactly the same manner (and this happens automatically) 10 of the 20 white layers have white right-hand neighbouring layers and the other 10 have black ones. The same can be said of the numbers of left-hand neighbours.

Partial ordering of the structure just described occurs if we begin to reduce the number of contacts of black with black and white with white layers. Such an alternation shown

in the last picture is not completely disordered. Of the 20 black layers, only 5 now have black layers as neighbours (either right- or left-hand). In other words, in three-fourths of the cases, the black layers have "proper" neighbouring layers. This means that the sequence has more order than disorder. The same is true of the white layers if we have an equal number of white and black layers. Thus, we are "halfway" from disorder to order. Order reigns when 20 out of 20 layers have "proper" neighbours, disorder when 10 out of 20 do, and in our case, there are 15 out of 20.

Alloys of a more complex composition pose more complicated problems when order and disorder in the arrangement of their atoms are considered.

Assume, for example, that the black layers amount to one-fifth of the total number of layers. Then the simplest ordered structure is, of course

○○○○●○○○●○○○○●○○○○●

Also feasible are superstructures, for instance:

○○○○○○○○●●○○○○○○○○●●

We should also distinguish structures of the type

○○○●○○●○○○○●○○○○●○○

in which no black layers have other black layers as neighbours. The number of white layers with black neighbours equals the number of black layers with white neighbours. What can we say about such a system of layers? It has no long-range order in the sequence of layers, but it has perfect short-range order with respect to the surroundings of the black layers. Information on them can be condensed and, consequently, we have elements of micro-order.

What arrangement is disordered in all respects?

We can reason as follows. Since the number of white layers is four times that of black ones, the number of white neighbours of the black layers should be, in the case of complete disorder, four times that of black neighbours of the white layers. A portion of such a disordered structure, singled out of an endless

sequence, may be, for instance,



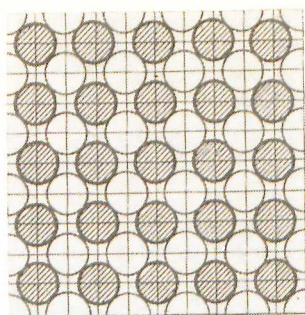
The 50 layers include 10 black ones. Of the 10 black layers only 2 have black layers for right-hand neighbours; the other 8 have white right-hand neighbours. Of the 40 white layers, 32 have white right-hand neighbours and 8 have black neighbours. The fraction of white neighbours of the black layers equals 0.8, and that of black neighbours of the white layers equals 0.2.

In contrast to the case when the numbers of black and white layers are equal, the ordering process in the last alloy may proceed in either of two directions. In the first place, the number of black neighbours may begin to decrease and the short-range order in the surroundings of the black layers may become ideal. But along with this, another process may occur: the emergence of long-range order, which can be conceived of as an equalization of the number of white layers confined between black layers.

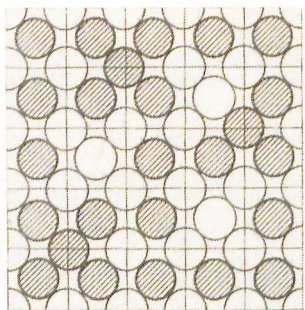
So far we have been discussing errors in the stacking of layers, and the reader may gather the impression that in crystal formation the atoms within the layers are necessarily arranged in order. Elements of disorder in order are more clearly defined in bodies consisting of regular layers of atoms. Disorder is far from being manifested "layerwise" in all cases, however.

Here, for instance, is the situation in alloys of iron and cobalt, having the simple body-centred cubic structure (Fig. 42). Each atom, whether iron or cobalt, has 8 nearest neighbours. The mutual arrangement of the centres of the atoms in a crystal of the alloy is always fully ordered. They always form the same body-centred lattice under any conditions. The distribution of the iron and cobalt atoms with respect to the sites they occupy is a different matter.

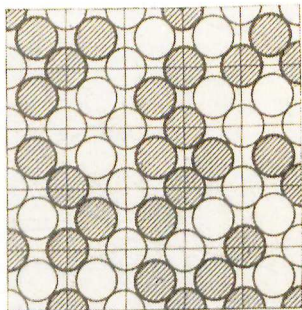
We can conditionally divide up the lattice sites of our crystal into corners and centres of the cubes. With complete order, all the corners are occupied, let us say, by iron atoms, and all the centres, by cobalt atoms. Perfect long-range order of such a crystal may gradually spoil, if we begin to find atoms occupying "someone else's" sites. However, as long as the number of atoms occupying their "own" sites differs from the number occupying "someone else's" sites, we are justified in stating that the crystal



(a)



(b)



(c)

Fig. 42. Atoms of an iron-cobalt alloy distributed among the sites of a body-centred cubic lattice. The white circles represent the iron atoms; the black circles, the cobalt atoms. The lattice sites can be filled with atoms of the alloy being investigated in different ways: (a) fully ordered alloy; all the "corners" of the cubes are occupied by iron atoms and all the "centres" by cobalt atoms; (b) long-range order is beginning to be impaired; (c) complete lack of long-range order.

has, even if only "spoiled", partial, macroscopic, but still, long-range order.

Long-range order disappears when there is no longer any difference between "someone else's" and one's "own" sites: half of the atoms are in their own and half in the other sites.

Of especial significance is the fact that when a crystal, built in a completely ordered manner, is heated, the order is gradually violated, i.e. the percentage of atoms occupying "someone else's" sites increases. It was found that there is a temperature above

which long-range order, even of the "spoiled", partial kind, cannot exist. This is known as the lambda point (from the Greek letter λ).

For iron-cobalt alloys, the lambda point is at 770°C. The transition from order to disorder indicates that thermal motion has overcome the "tendency" of atoms to become arranged so that long-range order is maintained.

There is much in common between the process of eliminating the difference between one's "own" and "someone else's" sites and the melting process. Both processes consist in the disappearance of long-range order. The difference is that in melting, long-range order disappears in the arrangement of the centres of the atoms, while in a transition at the lambda point, order disappears only in the arrangement of the atoms of various elements.

The main feature in the structure of iron-cobalt-type alloys is the possibility of partial long-range order, which can exist only with respect to the distribution of the iron or cobalt atoms, but not with respect to the arrangement of the centres of the atoms.

As in the case of melting, the destruction of long-range order does not imply the disappearance of order in general; short-range order remains.

With respect to the distribution of atoms in crystals of iron-cobalt alloys, short-range order consists in the "tendency" of cobalt atoms to surround themselves with iron atoms (and vice versa). If you take any atom and enumerate its eight nearest neighbours, you find that the number of atoms of the other element is not equal to one half of the total, i.e. 4. Depending upon the degree of perfection of the close-range order, an atom of iron can be surrounded, on an average, by five, six or seven cobalt atoms (Fig. 43).

Investigations of copper-gold alloys indicated that their short-range order is of a high degree of perfection and appears, not only in the number of nearest neighbours, but in the number of next-nearest neighbours as well, etc. If we construct, as previously, a number of spheres about any atom of gold, the first sphere includes, practically, only atoms of copper, the second, only atoms of gold. Further on, the perfection of short-range order is gradually violated, but a preference for the atoms of a definite element is felt as far away as the tenth sphere.

Very sophisticated investigations, conducted by means of X-rays, revealed how long-range order is "born" in the crystals of alloys.

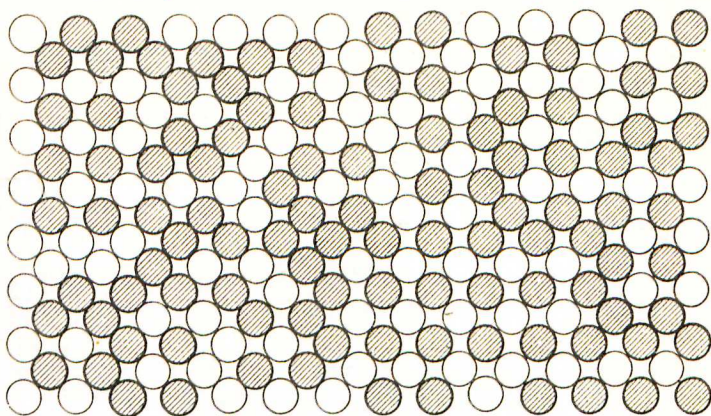


Fig. 43. Clearly defined short-range order and a lack of long-range order.

Experiments performed on cobalt-platinum alloys showed that regions of long-range order grow in a disordered crystal in the same way as stable nuclei of the crystal grow in the liquid (melt). These nucleating regions are located quite definitely with respect to the axes of the crystal.

Elements of disorder in order are frequently found in lamellar (layer) minerals: graphite, mica and chlorites. The structure of these substances obeys the laws we discussed above.

The phenomenon of volumetric disorder has been studied mainly in metallic alloys. Modern solid-state structure theory made it possible to clear up many important facts with respect to the forces that bind the particles in metals and in inorganic and organic substances. In inorganic crystals the bonding in a body depends upon the interaction between adjacent ions; in organic crystals, the interaction is between adjacent molecules. This is not the case in metals. Bonds between the particles comprising the metal consist mainly in the interaction between the positively charged ions and the negatively charged electrons. The latter travel in more or less free disorder within the lattice formed by the ions.

Thus, the essential distinguishing feature of a metallic crystal is the lack of definite bonds between the atoms.

This feature of metallic structure explains why deviations from perfect structure are especially frequently found precisely in

substances having metallic bonds. In fact, since each atom in a metal is "pooled" (in the sense that it has no particular "identity"), it can readily be replaced or displaced.

10. Magnetic Order

Short-range order, long-range order, order with respect to the arrangement of the centres of the atoms, order with respect to the distribution of the atoms of different elements, and these are still not all the possible kinds of "order". Two atoms of the same chemical element can differ in their other properties as well.

The best known difference between chemically identical atoms is in their weights. Every element can be obtained in the form of several so-called isotopes (from the Greek word meaning "same place", referring here to the place in Mendeleev's periodic table), which differ in the structure of their atomic nuclei.

Consider an alloy consisting of two isotopes of the same metal. From one point of view, this is not an alloy at all, but a pure metal. From another, it is an alloy in which all stages of order and disorder can exist with respect to the distribution of the different isotopes of the same metal. Hence, in addition to "chemical" order, substances may also differ in their "isotopic" order.

Even more interesting is their "magnetic" order.

Only a small number of substances have appreciable magnetic properties. They include iron, cobalt, nickel, gadolinium, compounds of these elements and some compounds of manganese and chromium. Since the main role in this family is played by iron, these substances are said to be ferromagnetic (*ferrum* being the Latin for iron).

What is so remarkable about the structure of these substances? What features in the structure of their atoms have granted them such exceptional properties?

The theory of atomic structure answers these questions in the following manner. Each electron possesses magnetic properties, like an unimaginably tiny magnetic needle. Most atoms have a tendency toward antiparallel arrangement of its "electronic needles". Taken together, such a pair of needles is deprived of magnetic properties like a pair of magnets lying side by side so that the north pole of one is flush with the south pole of the other. The only substances having noticeable magnetic properties are ones whose atoms include one or several uncompen-

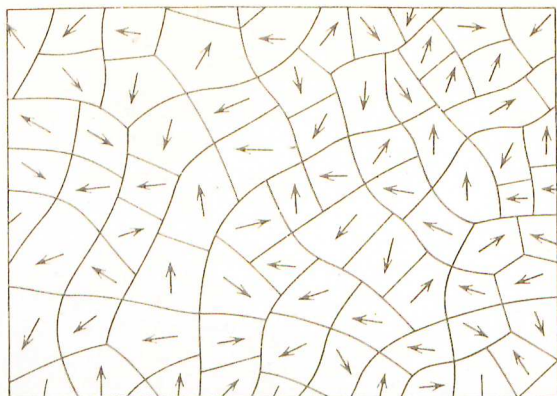


Fig. 44. Such a picture showing the arrangement of the magnetic needles of elementary magnets can be found in obsolete textbooks. It is incorrect.

sated "extra" electrons. The iron atom, for instance, has four uncompensated "electronic needles". As mathematicians say, however, this is a necessary condition, but not a sufficient one. To possess appreciable magnetic properties, a substance must contain regions consisting of millions of atoms whose "electronic needles" are oriented in the same direction. Such magnetically ordered regions are called domains. They can exist only in crystals.

It would be of interest to know why domains are formed in iron, for instance, but not in chromium, even though the chromium atoms, like the iron atoms, have magnetically unbalanced electrons. This is no easy question, and physicists will evidently have to carry on much more research before they find a comprehensive answer.

Until recently, the arrangement of the domains in a piece of unmagnetized iron was pictured as shown in Fig. 44. The arrows show the direction of the "electronic needles" of the atoms in the domain. It was supposed that when the piece of iron is magnetized, the domains turn so that the needles point predominantly in the direction along the magnetic field. The stronger the magnetization, the stricter the order obtained in the mutual arrangement of the domains.

Actuality, however, turned out to be much more interesting than this picture. Domains are sufficiently large to be seen under a microscope. But how can their boundaries be revealed? They are

not crystalline grains, nor even crystalline blocks. A completely homogeneous crystalline region may accommodate several magnetic domains.

Finally, a method was found. The piece of iron being investigated was "powdered" with a specially selected extremely fine magnetic powder. Since this powder is a magnetic substance its grains become located along the domain boundaries. Roughly speaking, each domain is a small magnet and its boundaries are the poles of this magnet. Well, as we know, magnetic powder is always attracted to the poles.

The first outstanding result of these investigations was the following. The order in the arrangement of the atoms in a crystal turned out to be closely related to magnetic order. The direction of magnetization of the domain is not a random one, but is related in a definite manner to the arrangement of the atoms in rows and layers.

This matter is especially simple in the case of cobalt. Crystals of cobalt consist of closely stacked layers according to the formula ...ABAB... (see Fig. 13). It has been shown experimentally that the domain needles of the crystal are always perpendicular to the densest layers. Hence the domain needles in a cobalt crystal point only in two opposite directions. If the crystal is not magnetized, there will obviously be as many needles pointing in one as in the other direction. How, then, does magnetization occur? Strange as it may seem, it occurs abruptly. All the "electronic needles" included in a domain, are suddenly reversed like soldiers upon the command "About face!" The stronger the magnetization, the greater the number of domains in which reversal occurs.

Obviously, a limit of magnetization must exist. It is reached when all the domain needles point in the same direction.

Another conclusion made on the basis of this research is that nothing will come of attempts to magnetize a crystal of cobalt in a direction along a layer of close packing. A magnetic field directed along the layer has no effect on the "domain needles" directed at right angles to the layer. An intermediate value of magnetization is obtained when the direction of the external magnetic field is oblique.

Naturally, what was said above does not concern finely crystalline cobalt, in which the tiny crystals and, consequently, domains are randomly arranged.

What can be said about iron, the chief representative of the family of magnetic bodies? Iron crystallizes into a cubic lattice. It was found that the "electronic needles" align most readily in the

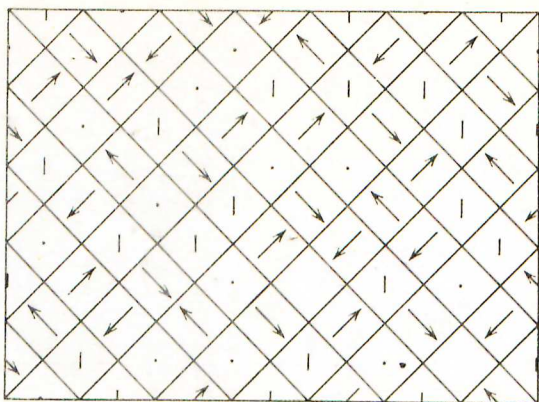


Fig. 45. This plane picture gives an idea of how the magnetic needles of the domains are arranged in an iron crystal. Dots and dashes indicate domain needles pointing to and from the reader.

directions of the axes of the cube. But there are six such directions. Corresponding to them are the six so-called directions of easiest magnetization along which the domain needles align.

To avoid complicating the picture with a three-dimensional representation, we have given a plane diagram in Fig. 45 which conveys an idea of domain structure in iron.

If we make use of the parallelogram method of vector addition to find the sum of all the little arrows, the answer for unmagnetized iron is zero. Magnetization consists in turning over the "electronic needles". This needle overturning does not necessarily have to take place in a whole domain at once. On the contrary, a more probable picture is the "consuming" of domains which violate magnetic order by the domains that are properly oriented.

The two photographs shown in Fig. 46 were taken with high magnification. You can see the surface of an iron crystal. It has been powdered with a magnetic powder to reveal the domain boundaries. As you see, the boundaries are straight lines. Above are the domains whose needles point to the right; below are those whose needles point to the left. The photograph at the right shows the same portion of the surface of the iron crystal after a magnetic field has been applied to it. What has happened? The applied field is directed to the right and therefore the "right-hand" domains have forced away the "left-hand" ones. The boundary between them has moved downward.

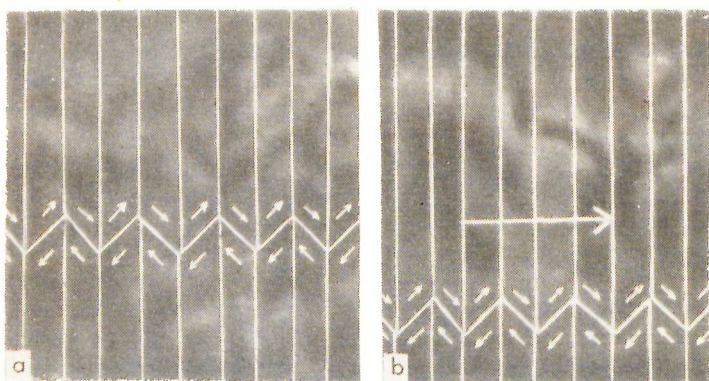


Fig. 46. The domain boundaries have been revealed on both photographs. As a result of the application of a magnetic field (at right), certain domains "consume" others.

There is much in common between magnetic order and order in the arrangement of the atoms, between crystalline blocks and domains. As we know, the transition from one crystalline block to the next is not abrupt, but extends over a certain "spoiled" region. Exactly the same is true of the boundary between domains. When carefully examined, this boundary is found to be, not

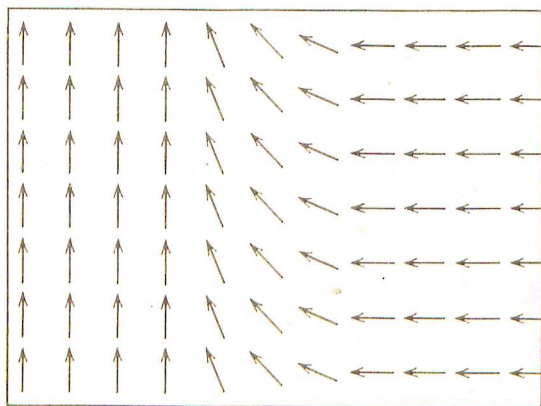


Fig. 47. Diagram of the transition layer between adjacent domains. Keep in mind that this is shown in a plane. Actually, the needles are turned in space.

a line, but a region in which the electronic needles gradually change alignment, from one direction of easiest magnetization to the other. Such a transition layer is illustrated schematically in Fig. 47.

Long-range order in atomic arrangement is destroyed at a certain definite temperature because the crystal melts. Temperature has precisely the same effect on the arrangement of the electronic needles. Beginning with a certain definite temperature, called the Curie point in honour of the noted French scientist, Pierre Curie (1859-1906), order in the arrangement of the needles disappears and the substance loses its magnetic properties. The Curie point for iron is at 768°C .

It has been established in recent years that long-range order in the arrangement of the electronic needles in the domains can be more complex than in the domains of iron or cobalt. In magnetic substances consisting of several kinds of atoms, it is possible for one group of atoms to have their magnetic needles aligned in one direction while those of another group are in the antiparallel direction.

It would seem that if one half of the needles point in one direction and the other half in the other, it would be impossible to detect this phenomenon. And it would be if the needles were arranged haphazardly. But it can be detected if we have magnetic order, even one in which half of the needles point in one direction and the rest in the other. All that is required is for the magnetic order not to coincide with the long-range order of arrangement of the atoms. We shall call the latter chemical order to distinguish it from magnetic order.

Shown schematically in Fig. 48 is the structure of manganese oxide. It is evident that the chemical lattice constant after which the structure is repeated is one half of the magnetic lattice constant. This difference can be detected by delicate experiments.

A peculiar example of magnetic substances with complex magnetic order are mixed oxides, for instance, a mixture of iron and nickel oxides. An iron oxide molecule contains two atoms of iron, and a molecule of nickel oxide, one atom of nickel. The crystal of the mixture is a close-packed structure of oxygen atoms with an atom of nickel and two atoms of iron filling the interstices. We know (from pages 34 and 36) that the empty spaces, or interstices, in close-packed arrangements may be of two kinds; tetrahedral and octahedral. An atom in an interstice of the first kind is surrounded by four nearest neighbours; an atom in an octahedral interstice is surrounded by six nearest neighbours.

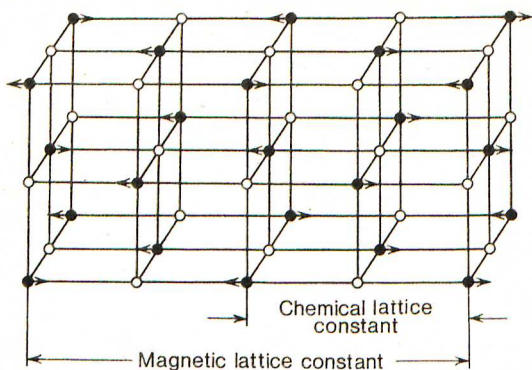


Fig. 48. Schematic diagram of the structure of a manganese oxide crystal. If we pay no attention to the arrows indicating the directions of the magnetic moments of the manganese atoms, the lattice constant (distance after which the structure is repeated) is only one half of the true constant. The smaller is the "chemical" lattice constant, the larger is the "magnetic" lattice constant.

It was found that iron atoms are distributed between interstices of both kinds. The magnetic needles of the iron atoms are oriented in complete order, but those of the atoms in the tetrahedral interstices point in one direction and those of the iron atoms in the octahedral interstices point in the opposite direction. As a result, the action of the two systems of needles is cancelled out. The magnetic properties of such oxide mixtures are provided by the magnetism of nickel whose atoms have their needles pointing all in the same direction.

Such remarkable substances are called ferrites. Their exceptional importance in engineering practice is that even though they have magnetic properties, they are electric insulators.

Chapter Five

Order and Disorder in the World of Giant Molecules

1. Long-Chain and Branched Molecules

First of all, what is meant by a giant molecule?

The largest molecules known to science today have dimensions of the order of tenths of a millimetre. In the world of atoms and molecules, this is an enormous value. Recall the size of atoms and the interatomic distances; they are about a single angstrom, i.e. one ten millionth of a millimetre. A line 0.1 millimetre long can accommodate a million atoms. If you consider that a giant molecule, in which the atoms are joined in tandem in a single direction, is about 3 or 4 angstroms wide, then its incredible length becomes evident. The length is greater than the width by several hundred thousand times. A rail of the kind used in railway has a thickness of about 10 cm. With the length-to-thickness ratio as that of a molecule of a million atoms, the rail would have to be 10 km long.

These figures set a record, but long-chain molecules of this type including hundreds of thousands, not to mention tens of thousands of atoms, are commonly found in nature and obtained in the laboratory. What kind of substances consist of such monstrous-sized molecules? These substances include rubber (caoutchouc), cellulose and certain biological molecules. Of huge length are the molecules of substances known by the trade names of Polythene, Capron, Nylon, and many, many others. Long-chain giant molecules are typical of high polymer substances or, for short, polymers.

Since we began with long-chain molecules, let us discuss them in more detail. We likened such a molecule to a rail. In another sense, this is not a very apt comparison. As a matter of fact, a rail is rigid and a molecule is flexible. We should have likened it to a rope, but hardly any ropes are of sufficient length.

It would be wrong to think of the flexibility of a molecule as of that of a willow switch. The molecule owes its flexibility to a remarkable phenomenon: the capability of parts of the

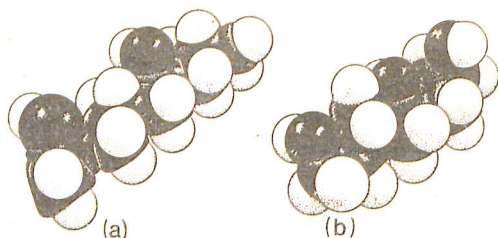


Fig. 49. Molecules of polyvinyl alcohol: (a) the molecule is stretched out; (b) the molecule is curled up. Bending of the molecule results from swivelling about the line joining the centres of the carbon atoms (black spheres in the drawings).

molecule to swivel about the bonds between the atoms. True, not all bonds allow such rotation, only the so-called single bonds (a single bond is the one that occurs when an atom has attached to itself the maximum possible number of atoms). In the great majority of molecules, however, there are more or fewer bonds of this kind and, accordingly, the molecule has more or less flexibility. Hence, the flexibility of a molecule could better be likened to that of a long mechanism consisting of a huge number of consecutive swivel joints.

Shown in Fig. 49 is a molecule of polyvinyl alcohol used in the production of artificial silk. We can see that the molecule consists of groups of atoms (seven atoms per group) repeated along a chain. The arrangement of the atoms in the molecule has a long-range order. If such a long molecule gets into a tangle, long-range order disappears. Depending upon the circumstances, flexible molecules can be stretched to their full length, twist and twine like a snake, or curl up into a ball. Figure 50 illustrates a model of a flexible molecule in these three positions.

Long-chain molecules are not the only members of the class of giant molecules. Molecules are found in nature or produced in the laboratory in which the bonds between the atoms are in all possible directions. In linear long-chain molecules, each group of atoms is joined to two other, "front" and "rear", groups. In a branched molecule, at least three paths lead from a given group of atoms to its neighbours. The tangled maze of bonds formed in some molecules produces a rigid system; such molecules cannot be flexible.

Branched molecules are found in such substances as formaldehyde resin, a widely employed solid plastic.

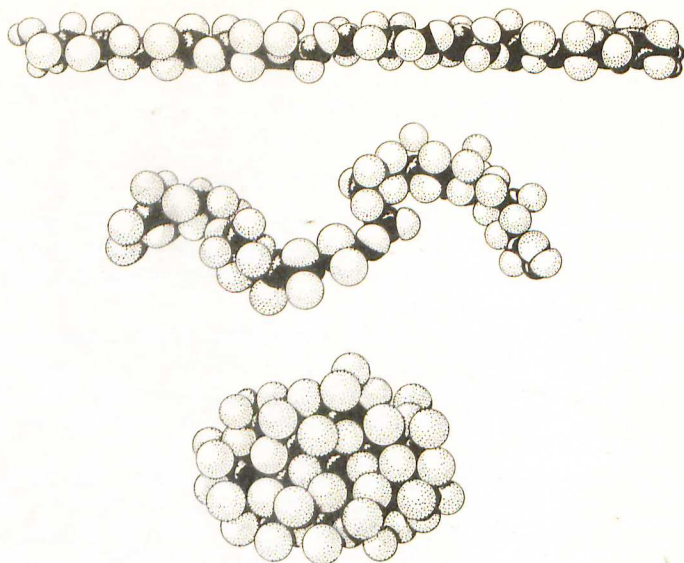


Fig. 50. Model of a flexible molecule in three positions.

The molecules discussed above do not, however, exhaust the list of different types of giant molecules. In recent years, scientists have learned to produce treelike molecules in the laboratory. They are something intermediate between long-chain and disorderly branched molecules. The word "tree" expresses the gist of the matter quite well. These molecules have a "trunk", which is a long-chain molecule, with branches sticking out of the trunk. True, the branches are usually of the same length; they do not taper down toward the treetop as in trees. In their turn, the branches can be attached in a greater or lesser degree by atomic bonds.

It is possible, therefore, to obtain giant molecules, intermediate between the long-chain and branched types, in an inexhaustible variety of shapes.

Most of the giant molecules have repeating groups of atoms. These are sometimes groups of a single kind, and sometimes (as in proteins) there is quite a large number of different groups. In the treelike molecules, one group of atoms may form the trunk and other groups, the branches. In a disorderly branched polymer, built of several groups of atoms, the groups are distributed at random. Long-chain molecules may have either

of two structures: with the atomic groups repeated regularly along the molecular chain, and with the atomic groups alternating along the chain without order. These factors may have a profound effect on the structure of the polymer.

2. Bundles of Long-Chain Molecules

Large as the polymer molecules may be, there are still millions and even thousands of millions of them in each minute fragment of nylon fibre or each tiny bit of rubber. How are these molecules packed in the substance?

We have seen many examples demonstrating that one of the basic tendencies in forming a solid and, for that matter, a liquid, is to close packing. Close packing of cumbersome and unwieldy molecules is no simple matter. How is nature coping with this task?

Thus, the problem is to closely pack flexible items. One feasible solution is to carefully wind each string into a ball and then closely pack the balls in exactly the same way as we packed the spherelike atoms in the preceding chapters. The other possible solution is to stretch each of the flexible items to its full length and to form something resembling a bundle of pencils. Any intermediate solution, i. e. packing without straightening out or without complete winding into balls, would not seem to ensure as close packing as the two first solutions, which are the only ones that make it possible to avoid complex tangling of the various chains, leading inevitably to a loss in density.

As a matter of fact, these are the ways that long-chain giant molecules are packed. In polymers we find the molecules either curled up in balls (coils) or stacked in bundles. (The preceding sentence is from the first edition of this book, but the reader will soon see that nature found still another way to cope with this problem.) In substances, manufactured in the form of artificial fibres, i.e. in the form of thread, the polymer molecules are arranged in bundles. Molecules, wound into tight coils (also called globules) are abundant in various kinds of protein bodies, such, for instance, as viruses.

But in what order are the molecules stacked in bundles and how are the bundles arranged with respect to one another? What happens to the concepts of long- and short-range order; crystalline and amorphous states? Haven't they lost their meanings when applied to polymers?

If we cut across a bundle of molecules, we see how the

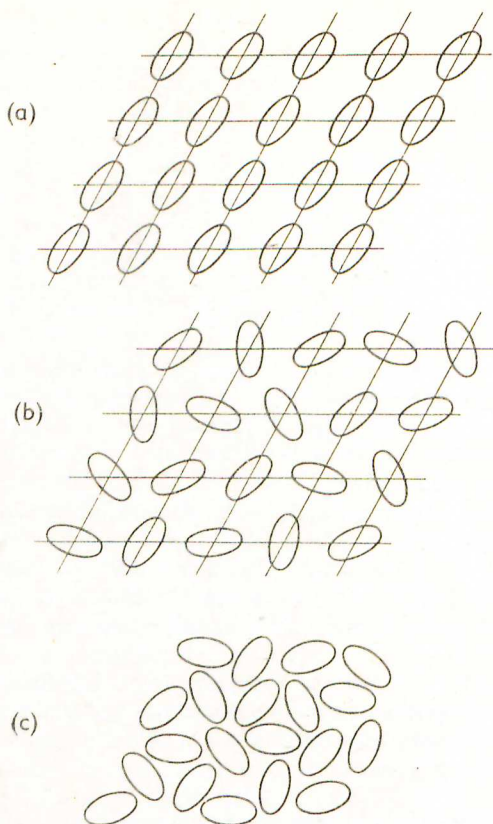


Fig. 51. Different kinds of packing of long-chain molecules with respect to the type of order. Three arrangements are possible: (a) complete order in the packing of the chains forming a crystal; (b) order in the arrangement of the centres of the cross sections and disorder in their orientation; (c) "liquid" arrangement of the molecules.

cross sections of the long-chain molecules are arranged. The cross section of these molecules may be of diverse and quite intricate shapes. But we are concerned only with the general problem of order within the bundle. We shall assume, therefore, that the molecules are cylinders of elliptical cross section.

The different arrangements of such chains of molecules (Fig. 51) are as follows. In the first arrangement (Fig. 51a), the centres

of the cross sections form a regular network and the orientation of the cross sections is ordered. This is a complete imitation of a crystal, i.e. it has long-range order. In the second arrangement, the centres of the cross sections remain as before, but their orientation is disordered (Fig. 51*b*). We can contend that there is long-range order in the distribution of the axes of the chain molecules and short-range order in the distribution of the chains with respect to their azimuth. Finally (Fig. 51*c*), there may be only short-range order with respect to the mutual arrangement of the chains.

In short, we can say that a bundle may have crystalline, gaseous-crystalline or liquid-crystalline ("liquid") stacking of the long-chain molecules.

This point of view on the structure of polymers was proposed by the author and checked by experimental research. It was found that all the three types of packing may be found in various polymers. Besides, all three types of order may be found in the molecules of a single polymer. Moreover, there are forcible arguments indicating that these different kinds of packing can succeed one another along a single bundle of chain-type molecules. The molecules frequently "tire" of marching along in neat files and, after a certain distance, they "relax" and "break step". Further on, the tendency toward order takes the upper hand again up to the next relaxation.

Do we have any data on the size of the bundles? Today we know that their thickness ranges from several hundred to a thousand angstroms. Changes in order along a bundle may occur after hundreds of angstroms.

3. Behaviour of Molecules with Bundle-Type Structure

We must frankly warn our readers that the picture of the structure, and more so the behaviour, of polymer substances consisting of long-chain molecules, is substantiated to a much lesser degree than the information we have presented about crystals. However, it is not so much a matter of substantiation as the fact that different polymers behave differently. One must therefore be careful in formulating a general law of nature.

One of the possible ways in which the bundles may be arranged in a solid polymer is shown schematically in Fig. 52. It is stressed here that the bundles are sufficiently flexible and can turn every which way, bend and even curl up. To some extent, the individual properties of flexible molecules have been imparted to the collective body, the bundle.

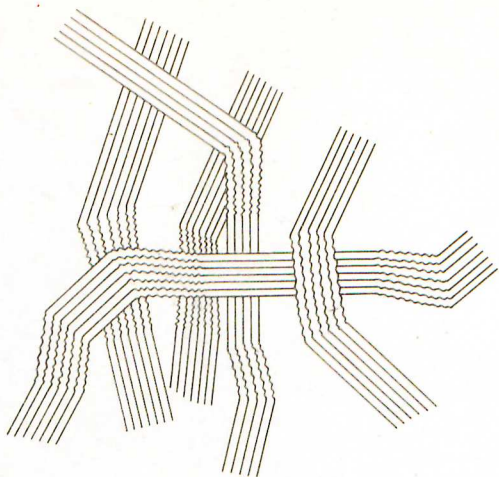


Fig. 52. Bundle-type model of a polymer.

It is difficult to illustrate in the diagram how closely the bundles adjoin one another. There are, of course, transition regions between neighbouring bundles.

It is obvious that the behaviour of bundles, mentioned in the title of this section, covers an extensive range of problems. We shall consider only their thermal and mechanical properties.

The majority of polymers undergo a number of changes in structure before they finally melt. In fact, heating increases the degree of disorder, but in a polymer there are so many intermediate stages between order and disorder that heating to various temperatures "introduces" various kinds of disorder, one after another.

At low temperatures most regions of a bundle are of a crystalline nature, but, as it is heated, transformations occur associated with the beginning of rotation of certain parts of the molecules, then with the conversion of crystalline regions into gaseous-crystalline ones and, finally, with the conversion of regions of the bundles to the regions of liquid structure. To know the melting point is of little aid in describing the thermal behaviour of a polymer.

If the initial polymer has no crystalline regions, no melting takes place. Such a polymer softens gradually, and its behaviour can be likened to that of ordinary amorphous glass.

The mechanical properties of polymers with bundle-type structure,

which may include rubber, and polythene and ... even wood, are also strikingly diverse.

Where does rubber get its amazing elastic properties that enable a rubber band to be stretched to five times its initial length and then return exactly to its previous state when it is released? What happens to the molecules in such reversible extension? It seems quite probable that the bundles of rubber molecules are wound in the same way as the coils of mooring ropes you see lying on the deck at the bow or stern of a steamship. Then extension corresponds to the unwinding of such a coil. The curling of bundles into coils should take place over relatively large areas since experiments indicate that a bundle cannot be tightly bent within 100 to 200 angstroms.

Scientists are continuing an intensive search for new kinds of artificial rubbers and a study of their structure. To be sure, no one doubts today that the struggle between order and disorder is responsible for the inimitable properties of rubber.

Electron microscopy has played a crucial role in clearing up the structural details of these remarkable substances. The eye of the electron microscope has converted all our hypotheses on order and disorder into indisputable facts.

To prevent the reader from accusing me of rehashing long-known matters, I can cite an interesting example. A section through a new kind of rubber is shown in Fig. 53. This substance possesses outstanding properties and is made up of polymer molecules (or, more exactly, pieces of molecules) of styrene and butadiene (divinyl). If this substance is extruded through a fine die opening, an exceptionally interesting structure is produced. It consists of long cylinders of the polystyrene polymer distributed in a continuous mass of polybutadiene. The white circles in the photograph are cross sections of the polystyrene molecules, of a shape almost cylindrical. The polybutadiene forms the continuous background.

This does not imply that polymers consisting of scraps of molecules of two kinds always produce this type of structure. The feasible versions are truly inexhaustible. But they have one factor in common: a combination of order and disorder.

A few words on rubber are appropriate at this time. Many readers, not versed in engineering or chemistry, may think that rubber and caoutchouc (as crude rubber is sometimes called) are almost one and the same thing. Nothing of the kind. Many think that the natural colour of rubber is black. Actually, natural caoutchouc, or latex, of which rubber is made, is a light-coloured,

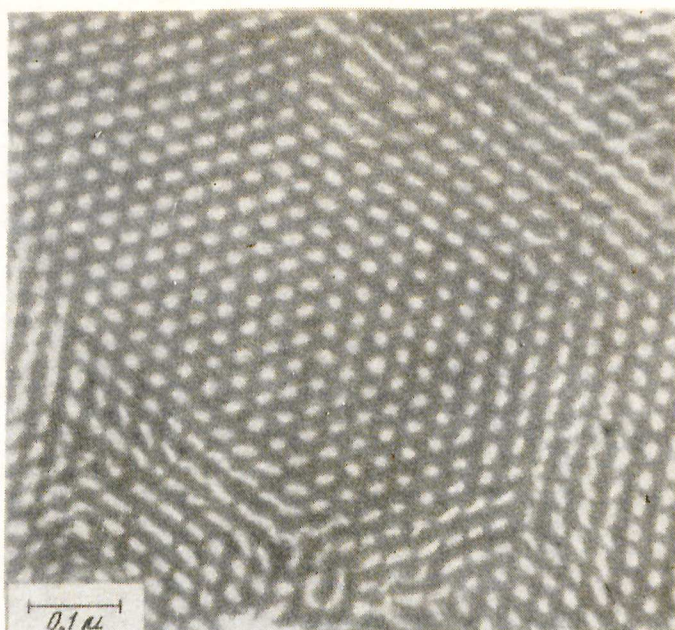


Fig. 53. This material is said to be composite. It is a new kind of rubber consisting of polystyrene and polybutadiene.

milky liquid. To impart to rubber strength and elasticity, the crude product, caoutchouc, is vulcanized (cured) with sulphur or other curing agents. As a result, a network of chemical bonds (called sulphur bridges) is formed and the material acquires the properties we associate with rubber.

But this is not enough. Such cured rubber is still weak and quite unsuitable for practical application. The rubber is strengthened by adding soot, commonly called black or carbon black. Black is an active filler (reinforcer) of rubber and drastically improves its mechanical properties (strength and others).

Black (soot) can be graphitized. This is done by heating to 2000°C . Besides improving the mechanical properties, graphitized black imparts other unique qualities to rubber, namely, the possibility of obtaining an electrically conducting material. Incidentally, rubber filled with graphitized black is used to make the earthing strip, or "tail", we see hanging behind our Lada passenger car to discharge static electricity.

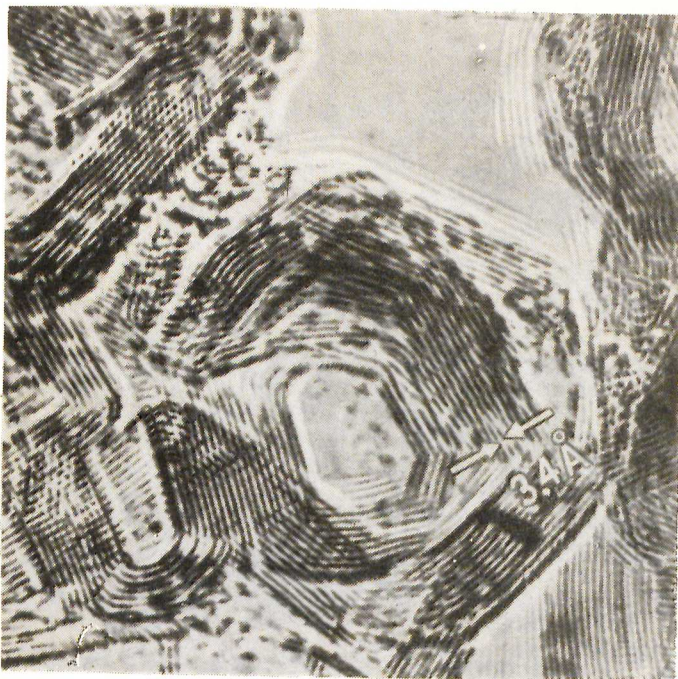


Fig. 54. A photomicrograph of carbon black (soot) demonstrating the close relationship between black and graphite.

How did we find out that black (soot) acquires the properties of graphite? The answer is given in Fig. 54. We see that black is actually converted into graphite from the fact that the distance between the atomic planes equals 3.4 angstroms, which is the same distance we find in graphite, whose structure is illustrated in Fig. 19*b*.

4. Monocrystals of Folding Polymer Molecules

A breakthrough that has led to a more comprehensive study of the fundamentals of high-molecular structure was the discovery by means of electron microscopy of neat, well-formed crystals, first on polyethylene (in 1957) and later on other linear polymers. Note that the model consisting of tangled chains is incompatible with the formation of faceted monocrystals. In fact, the regular

geometric shape of a monocrystal serves as the external indication of its strictly regular internal order in the arrangement of the atoms or molecules of which the crystal consists. Therefore, specialists in this field have long considered the impossibility of their forming faceted monocrystals to be a specific feature of high-polymer substances. The discovery of monocrystalline forms in linear polymers aroused much interest and attracted the attention of investigators.

Before discussing the monocrystals of linear polymer molecules, it is of advantage to look into the structure of the monocrystal of normal paraffins, which are low-molecular chain-structure substances.

What draws our attention to the monocrystals of normal paraffins? The point is that the main difference between the molecules of normal paraffins and those of linear polyethylene is that the former are shorter. A crystal of a normal paraffin, whose electron photomicrograph resembles the picture in Fig. 69 *c* (actually, they are alike as two peas), is made up of molecules in a zigzag chain consisting of 36 atoms of carbon. This crystal is built of thin layers which seem to coil in a low-pitch conical helix about an invisible axis and impart a stepped appearance to the whole surface. It has been established that the molecular chains do not lie in the plane of these layers, but are vertical with respect to them. Moreover, the thickness of one layer is about equal to the length of a single molecule of paraffin (Fig. 55 *a*).

If a small amount of polyethylene is dissolved in a hot solvent and conditions are provided for slow cooling of the solution, extremely fine crystalline particles, clearly visible under an electron microscope, are precipitated. The monocrystals of polyethylene turned out to be astonishingly like monocrystals of

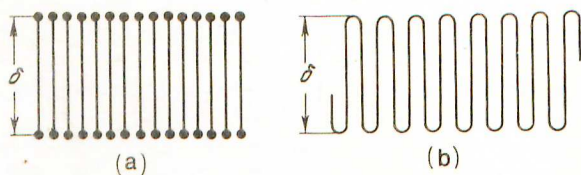


Fig. 55. Thickness δ of a single layer: (a) in paraffin; (b) in polyethylene. To simplify the drawing, the zigzag shape of the chains is not shown.

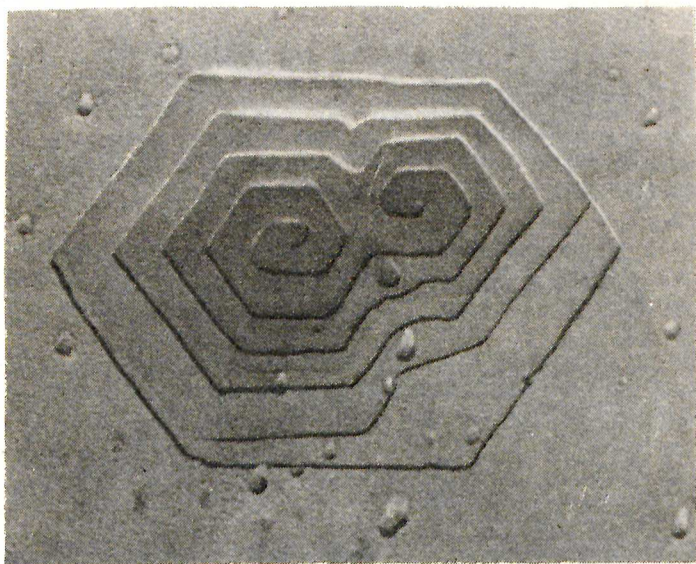


Fig. 56. Electron photomicrograph of a polymer crystal. Magnification: $\times 35000$.

normal paraffins, having the same rhombic shape and consisting of separate layers. Though of somewhat less perfect shape, they still displayed sufficiently good faceting. The layer thickness was found to be constant, equal to 100 to 120 angstroms in all the experiments (Fig. 56).

It was established, as with paraffin, that the molecular chains of polymers are perpendicular to the plane of the crystalline plate and, consequently, to the plane of each of its component layers. As mentioned, in paraffins the layer thickness is determined by the length of the molecules. How then can we picture the structure of a single layer of polyethylene whose thickness was found to be only 100 to 120 Å and whose molecules in the investigated specimens had a length of 6000 Å?

There is only one feasible explanation: the molecules of polyethylene in the monocrystal are of "folded" configuration as is shown schematically in Fig. 55*b*. Here the thickness of each layer is approximately equal to the distance between two consecutive bends in the hydrocarbon chain.

In the course of further research, "folded" configuration of molecules that are in the form of monocrystals or in other modes

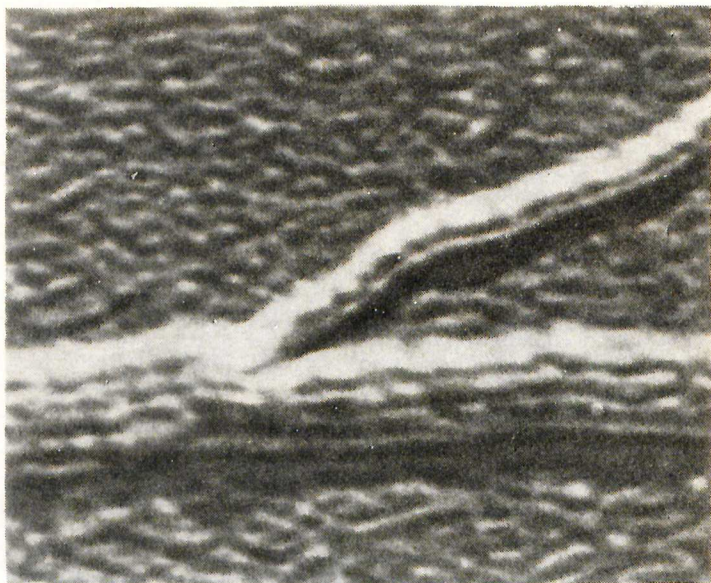


Fig. 57. An electron photomicrograph. Lying on the backing film is a ribbon consisting of separate polymer filaments. Magnification: $\times 300\,000$.

(for example, filaments, as in Fig. 57) was discovered in other linear polymers as well.

5. Structure of Polymers

Among the immense variety of articles manufactured from artificial fibres and plastics that the up-to-date chemical industry supplies us with, we find three types of structure: bundle (chain-packed), globular and branched.

We have just discussed polymers with bundle-type structure in sufficient detail. Rubber, cellulose, capron and perlon are only the chief representatives of this structural class.

Globular structure is frequently found in proteins. Look at the photograph of the tobacco mosaic virus in Fig. 58. The exceptional degree of order of this substance is quite obvious. True, this does not imply that we are dealing with a genuine crystal. The fact is that order in such substances may not extend to the atoms

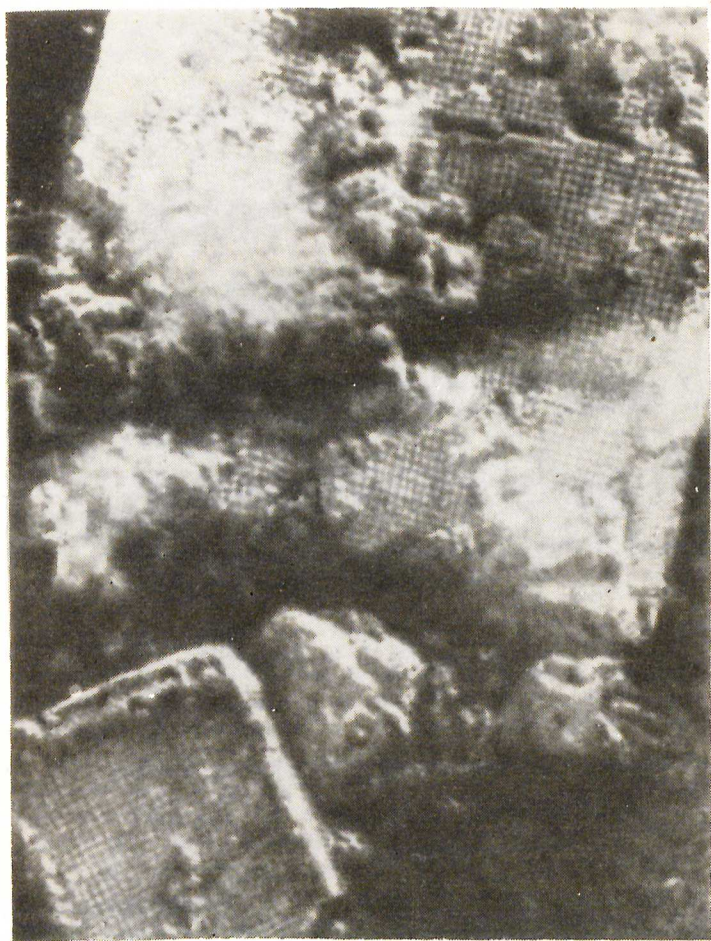


Fig. 58. Electron photomicrograph of the tobacco mosaic virus.

in the molecules or, in any case, inside sufficiently large atomic groups. Sometimes such crystals can be likened to sacks of potatoes stacked in strict order. The centres of the sacks form a regular lattice, but the potatoes within each sack have their own peculiar order (or disorder).

Polymers of the third class are thickly branched systems. They belong to the class of amorphous substances, and have

no short-range order. We have already discussed molecules of this kind. In this, however, we were probably slightly inaccurate. When molecules of this kind form a solid substance, for instance, a piece of plastic, the concept of a molecule loses its meaning. The atomic groups are bonded continuously and it is impossible, even mentally, to pass an interface between two adjacent "molecules". The situation is similar to that mentioned in discussing crystals of the common salt type.

Before we began our acquaintance with polymers, we were informed on matters that substantially shook our belief in the possibility of dividing solids into amorphous and crystalline substances, but did not completely destroy it. We found elements of order in disorder and elements of disorder in order. But, nevertheless, we were concerned with disturbances and violations, while the basic feature of the classification remained inviolable.

Now the picture has changed essentially. Simple and clear terms, crystalline and amorphous substances, turn out to be insufficient to describe the structure of polymers. Nor can we find a way out if we approach the problem like a bookie, figuring out the percentage of crystallinity in each polymer.

Our conclusion on the structure of these unique substances is of a different nature: in various types of polymers we find combinations of different degrees of order of the molecules. The word "order" and "disorder" must be more precisely defined if we want to describe the structure of polymers correctly. Order, ... in what? If we mean the arrangement of the axes of the chain-type molecules, we can find such order in all polymers of bundle-type structure. If we mean order in the arrangement of the cross sections of the chains, there may be three kinds of such order, and all three may be found in a single substance. Disorder, ... in what? It may be in the arrangement of the atomic groups along the chain, or in the orientation of the bundles of molecules.

Evidently, as we can see, one or two words are insufficient to describe the structure of polymers. It often proves impossible to simply classify a polymer as a crystal, amorphous body or a mixture consisting of amorphous and crystalline fragments. In the world of substances made up of giant molecules, an immense variety of different cases can be found, from perfect long-range order to its complete absence. As for short-range order, it is always present in polymers. All in all, with respect to order, a polymer is in no way "inferior" to a liquid.

6. The Living Cell

Animal and vegetable tissues consist of cells. The cells of various animals and plants, and what is more, the cells of different tissues of the same organism, differ drastically from one another. Still, all cells have certain common features.

A cell is a sufficiently independent formation. Its matter is enclosed by a membrane about a hundred angstroms thick. Swimming in the liquid matter of the cell, the protoplasm, are its solid parts: the cell nucleus, chloroplasts in the cells of green plants and mitochondria. All these corpuscles look like small grains under a moderately strong microscope. There have been spectacular advances in recent years in studying the structure of these tiny grains; their purpose was discovered.

A living cell is a most intricately organized and automatically operating factory. The cell prepares substances required by the organism; the cell receives and fulfils commands to accomplish necessary movements. To carry out these functions, the cells require energy. By means of the chloroplasts they extract this energy from the sun's rays; by means of mitochondria, from nutritious substances. Commands for producing molecules needed by the organism come from the cell nucleus. This nucleus also contains genetic material which is transmitted from cells to their heirs upon cell division.

Any particular details on the mechanism and functioning of living cells are beyond the scope of this book. Here we are investigating the structure of matter from only one point of view: order and disorder in the arrangement of its particles. And only to this do we draw the attention of our readers. The drawings of cells found in old biology textbooks did not arouse the fantasy of physicists studying the structures of matter. Before the advent of electron microscopy with its capacity to magnify the object being observed by tens and hundreds of thousands of times, the living cell seemed to be a disordered collection of corpuscles. New research revealed a high degree of order in the arrangement of the various tiny grains that compose the cell.

Look at Fig. 59. This is what the power station is like in a living cell. It converts solar energy into the mechanical, chemical or electrical work required by the organism. The chain-type molecules that transform light into work are molecules of a substance called chlorophyl. A cell requires many molecules of this kind. The process of converting energy would be extremely

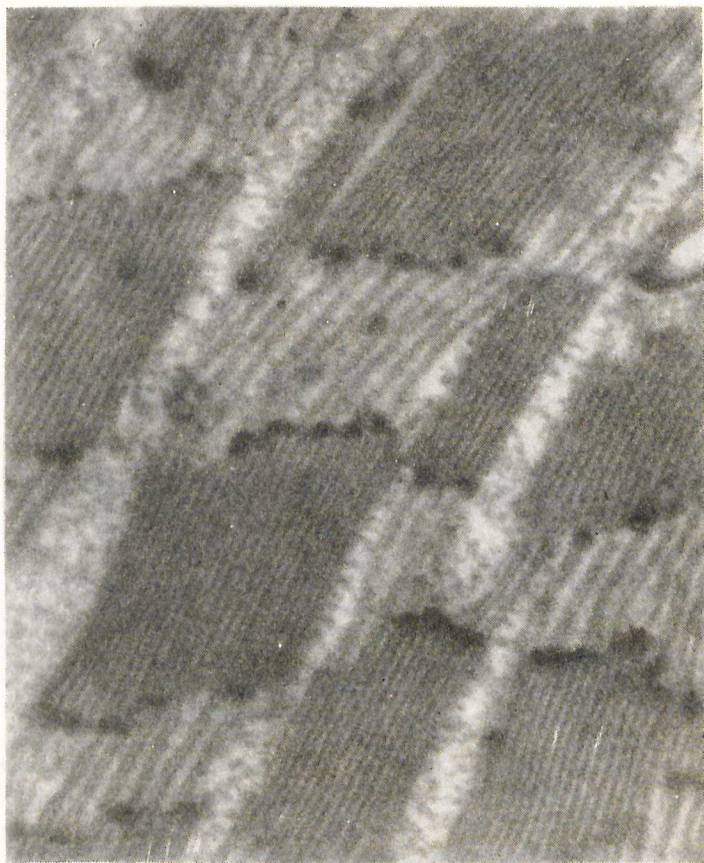


Fig. 59. Electron photomicrograph of chloroplast. Magnification: $\times 90\,000$.

difficult, and maybe impossible, if these molecules were simply strewn about haphazardly in the cell. Nature creates ordered designs. The molecules of chlorophyll are sandwiched between layers of fats and proteins. These are the layers you see in the illustration. The system consists of separate stacks of such layers. Evidently, such an arrangement provides more safety. If one stack gets out of order, others will continue their useful work.

The second photograph to which we draw your attention is,

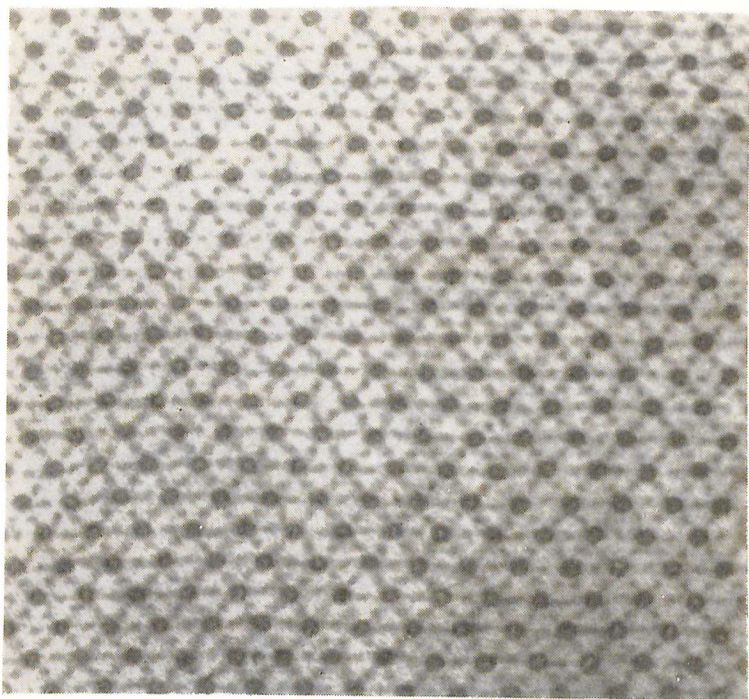


Fig. 60. Electron photomicrograph of the cross section of a muscle fibril. Magnification: $\times 250\,000$.

perhaps, even more amazing (Fig. 60). What is it? Maybe it is a metallic crystal and the black dots are its atoms? Nothing like it. You see the cross section of a wing muscle of an insect. It appears that the muscle is made up of two kinds of fibres (protofibrils): thick ones, seen in the photograph as large dark spots, and thin ones, which are the lighter spots of smaller size. Both kinds of fibres are arranged with a high degree of order. The law of their arrangement (hexagonal motif) indicates that we have here something like the gaseous crystalline state discussed in Chapter 4. The axes of the fibres form a regular lattice, but the orientation of the molecules comprising the fibres is entirely disordered (this random orientation is demonstrated by physical research). Here, again, there is good reason for the ordered arrangement of the particles. According to a widely accepted



Fig. 61. Photomicrograph of the longitudinal section of a muscle.

hypothesis, muscle contraction is accomplished by the sliding of the thin fibres with respect to the thick ones: one system seems to move into the other. Such a mechanism would be obviously impossible without ordered arrangement.

For those who doubt this version of muscle operation, we offer another electron photomicrograph (Fig. 61). This time it is a longitudinal section through a muscle. True, it is not the same muscle, but that does not matter here. The high degree of organization of matter in muscles is beyond any reasonable doubt.

The photomicrograph in Fig. 62 gives us an idea of what a nerve fibre looks like. This is a cross section of the central nerve fibre running from the optic thalamus of a mouse to its eye. This photograph (of a quality still far from what could be desired) means much to a biologist. In the first place, we see that the axon, along which the nerve impulses travel, is wrapped in a mielin sheath which consists of alternating layers of proteins and lipids. Arrow 1 indicates the place where the spirally wrapped mielin sheath contacts the membrane of the axon. Arrows 2 show the merging of two adjacent cells.

Finally, still another photograph, which, in my opinion, demonstrates an absolutely staggering degree of order in living



Fig. 62. Cross section of a nerve fibre.

matter. In Fig. 63 you see the structure of the lipid sheath in the wall of a newt's eye.

Today, electron microscopy has made tens and even hundreds of thousands of splendid photographs, with a resolution of several



Fig. 63. Sheath of the wall in a newt's eye as seen under an electron microscope. Magnification: $\times 210\,000$.

angstroms, available to the biologist, enabling him to examine the structural details of living tissues.

The author is convinced that in the near future electron microscopy will make it possible to examine the atomic structure of living tissues as well. The significance of this breakthrough cannot be overrated. The author, however, has neither the opportunity nor the necessary specific knowledge to continue this fascinating subject. Our aim was only to prove that the problem of order and disorder in the arrangement of atoms and molecules is directly concerned with biology.

Order $\rightleftharpoons$ Disorder Transformations

1. Iron Vapour and Solid Air

Strange combinations of words, are they not? This is not nonsense, however. Both iron vapour and solid air actually exist in nature, but not under ordinary conditions.

What are the conditions that we have in mind? Observations show that the state of matter is fully determined by two factors: temperature and pressure. Physicists call these two quantities state variables.

Life exists on earth under comparatively invariable conditions. The air pressure varies within only several per cent about an atmosphere which is equal to a pressure of one kilogram per square centimetre. The temperature of the air, say in the vicinity of Moscow, ranges from 30°C below zero to plus 30°C. In the absolute temperature (Kelvin) scale, in which zero is the lowest possible temperature (-273°C), this range of Moscow temperatures is less impressive: from 240° to 300°K, which also constitutes only several per cent of the mean value.

We are, quite naturally, accustomed to these ordinary conditions and therefore, when we state simple truisms, such as "iron is a solid", "air is a gas" and others, we forget to add: under standard conditions.

If we heat iron, it first melts and then vaporizes. If you cool air, it first turns into a liquid and then solidifies.

Even if the reader has never seen iron vapour and solid air, he probably will believe without any difficulty that by changing the temperature any substance can be obtained in the solid, liquid or gaseous state or, as they also say, in its solid, liquid or gaseous phase.

This is easy to believe because there is one substance, without which life would be impossible on earth, that everyone has seen in the form of a gas, as a liquid and as a solid. We have in mind, of course, water.

Under what conditions is a substance transformed from one

state to another? Phase transitions* are transformations from order in the arrangement of the atoms to disorder and vice versa. It is a direct aim of this book to discuss the rules for these transformations.

Let us first consider evaporation, the transition of matter from the liquid to the gaseous state.

Evaporation consists in the escape of molecules from the surface of a liquid. This may happen to a molecule receiving a sharp chance blow in collisions with its neighbours. The blow must be quite heavy in order to accelerate the molecule to a sufficiently high velocity. Only such molecules, travelling at highest speeds, are capable of overcoming the binding forces that hold them in the liquid.

It can be readily understood, then, why an increase in temperature speeds up evaporation. The higher the temperature, the more intensive the molecular motion. Consequently, the molecules at the surface are subject to more frequent and stronger pushes in the outward direction delivered by the molecules in the liquid.

There is one more conclusion, excellently confirmed by experiment: when a liquid evaporates, the fastest molecules escape. This means that the average velocity of the molecules remaining in the liquid is reduced. But this, in its turn, means a lowering of the temperature. If the temperature of an evaporating liquid is maintained constant, there must be a continuous transfer of heat to it from outside.

Recall the cold you feel coming out on the shore after swimming in a river. The reason is that the evaporating water takes heat from you. When evaporation takes place in the open air, the escaping molecules depart on a long journey. They are followed by another portion of molecules, then still another, and this continues until the last drop of liquid is gone.

Some substances evaporate at a high rate, before your eyes. Ether, under ordinary conditions, is one of them. Other substances may evaporate for days or even years. It all depends upon the relationship between the intensity of thermal motion of the molecules and the binding forces keeping the molecules together.

It is quite another matter when evaporation takes place in a closed vessel or even in a room with tightly closed windows and doors. But this is also a well-known fact. We often express our annoyance, saying: "The eau de Cologne has evaporated because someone forgot to close the bottle with the stopper". Why does evaporation cease in a partly filled bottle closed with a tight stopper? The reason is this. As evaporation proceeds,

the number of molecules of vapour increases. But now the molecules do not leave "for parts unknown". They continue their random movements immediately above the surface of the liquid. From time to time, molecules travelling toward the liquid are captured by it and return. The more molecules accumulated above the liquid, the more frequently such captures occur. Finally, the number of molecules escaping every second from the liquid equals the number returned to it in the same time. This sets up a state of equilibrium between the liquid and its vapour. In other words, evaporation stops. The vapour and the liquid peacefully coexist, exchanging molecules.

This state of equilibrium is also called the state of saturation of the air (or other gas) above the liquid.

For some liquids, the state of saturation occurs after much substance has evaporated; for others, when the amount is small. In short, the density of saturated vapours may have a wide range of values.

At room temperature the density of saturated water vapour is about 0.00002 g/cm^3 , and that of mercury vapour is $0.00000001 \text{ g/cm}^3$. A room of medium size (tightly closed, of course) with a floor area of 25 m^2 and a height of 4 m can accommodate as saturated vapour 2 kg of water or only 1 gram of mercury.

This means that if we have spilled up to two litres of water over the floor of our room, the puddle will dry after a certain length of time because the water will evaporate. If we put a whole barrel of water into the room, again only two litres of water evaporate, regardless of the volume of the barrel.

The same is true of mercury. Mercury vapour is very harmful and is a health hazard. When working with mercury, you must be very careful not to spill any, even a drop. Note that if you spill a whole glass or let only a drop weighing about one gram escape, the harm you do is the same. In either case, one gram of mercury is converted to the gaseous state.

The danger of mercury poisoning can, of course, be drastically reduced by applying intensive ventilation. Our discussion concerned a room tightly closed like a bottle of perfume.

When, a bit earlier, we spoke of evaporation in the open air, we were not quite exact. Open-air evaporation would never end if it were not for the force of gravity exerted by the earth on all bodies, including, of course, molecules of vapour. In dealing with the evaporation of large masses of water, this attraction cannot be neglected. In this respect, the behaviour of

the water vapours in the air resembles the conditions in a closed room. Air is always mixed with water vapour and, very often, to the point of saturation. We readily understand now why the water in a glass does not evaporate.

Let us return to evaporation in a closed vessel. Assume that evaporation has ceased and the vessel contains liquid and saturated vapour. Let us close the vessel with a piston, rather than a plug or stopper, and move it inward. The liquid is practically incompressible and, consequently, we compress the vapour and its density increases. But the vapour had already reached its limiting value because we had saturated vapour before compression began. Saturated vapour is in equilibrium with the liquid; the number of molecules escaping from the surface of the liquid is equal to the number returning to the liquid. No need to prove that when we increase the density of the vapour, we violate this equilibrium. The number of returning molecules exceeds the number of evaporating molecules. The amount of vapour is reduced or, as we say, the vapour condenses.

If we continue to reduce the volume, we can convert all the vapour above the surface into liquid. The opposite is also true, of course. If we pull the piston outward, we provide more and more volume for the saturated vapour. We could, in this way, convert all the liquid to the gaseous state. As long as a single drop of liquid remains in the vessel, the density of the vapour remains the same (because it is saturated). If we pull the piston still farther out, we provide excess space for the vapour, which becomes unsaturated. Then its density (and, consequently, its pressure) is reduced.

It is evident from this description that if we compress a gas at constant temperature, we can finally obtain a liquid.

We have already mentioned that a liquid evaporates more quickly when we raise the temperature. If evaporation occurs in a closed vessel or room, the temperature is related to still another important circumstance. As we raise the temperature, the density of the saturated vapour and, consequently, its pressure are increased. Why does this happen? Consider a vessel in which the liquid is in equilibrium with its vapour. We begin to heat the vessel. The velocity of the molecules increases in both the liquid and the vapour. But this has a significant effect only on the behaviour of the molecules in the liquid. They escape more easily from the surface. As to the vapour molecules, their higher velocities lead to no substantial increase in the number of molecules that become attached to the liquid. At whatever speed the molecule travels toward the surface of the liquid, the result is the same:

when it touches the surface, the molecule becomes a part of the liquid. In exactly the same way, a fly sticks to fresh flypaper, regardless of whether it carefully lands on the paper or dives into it at full speed.

Thus, when we raise the temperature, we shift the equilibrium between the vapour and liquid in favour of the vapour. The density of the saturated vapour increases.

We already know about the difference in the arrangements of the molecules in a liquid and a gas. In liquids the molecules are arranged with short-range order; in a gas they are in complete disorder. Is this actually a fundamental difference? The two phase states differ only because of their different densities. If the molecules are brought closer together, short-range order in their arrangement becomes more and more distinct. And what if the density of the vapour is increased to that of the liquid? Then, evidently, there will be no difference between the gas and the liquid. But can we obtain such a gas?

Take a vessel which is almost filled with a liquid. We close the vessel tightly and begin to heat it. The small free space above the liquid is rapidly filled with vapour, which is saturated. If we continue heating, the density of the saturated vapour will keep increasing. Finally, we inevitably reach a temperature at which the density of the vapour becomes equal to that of the liquid. No instruments of any kind are required to mark this point. At the critical temperature, as it is called, the line marking the free surface of the liquid disappears so that there is no longer any boundary between the liquid and the vapour.

Let us raise the temperature a little higher. Consider, now, the properties of the substance which is now at a temperature above the critical value. Assume that the experiment just described was conducted in a vessel with a piston. We pull out the piston and the volume of the gas (or, if you wish, liquid; there is no difference) increases and the density falls. We continue to pull out the piston. The density of the substance drops so low that we can no longer call it a liquid. It is now a gas and its molecules are in complete disorder.

Now recall what was stated on the preceding pages. By increasing the pressure of a vapour we can bring it to the saturated condition and obtain a liquid. Does this statement still hold? By pushing in the piston we can compress the gas to exceptionally high densities at which the molecules are arranged in short-range order. Everything is all right; we have obtained a liquid. Is this actually so?

Now, please, pour the liquid from the experimental vessel into a glass. To do this, you must first remove the pressure. But while you pull back the piston, the density of your liquid (or gas) continues to fall, our gain (short-range order) is lost, and you will not succeed in pouring the substance into the glass.

Hence, the conversion of a gas into a liquid that you can pour into a glass is possible only at a temperature below the critical one.

The lack of knowledge of the existence of critical temperatures led to the failure of early attempts to liquefy such gases as oxygen, nitrogen and hydrogen. The critical temperature of nitrogen is 146 C below zero; those of oxygen and hydrogen are 118 C and 240 C below zero. There is only one way to convert these gases into liquids: their temperatures must be lowered below these critical values.

The reader must have noticed that we have used the words "gas" and "vapour", almost without distinction, for a substance whose molecules are arranged in complete disorder. As a matter of fact, these two words have almost the same meaning. We can say that the gas of water is water vapour, or the gas oxygen is the vapour of liquid oxygen. Nevertheless, a certain tradition has been established for the use of these words. Since we are accustomed to a definite, comparatively narrow range of temperatures, we commonly employ the word "gas" to describe substances whose critical temperature is substantially below the temperatures we are familiar with. On the contrary, we speak of a vapour when the substance exists in two phase states, as a vapour and as a liquid, in our customary environment.

When we say a "substance evaporates", we ordinarily mean that a liquid evaporates. But solids can also evaporate. This is sometimes called sublimation. One of the best known examples of the evaporation of a solid is the sublimation of naphthalene, of which moth balls are usually made. It is precisely this property of naphthalene that makes it suitable to repel moths from clothing. A fur coat, protected by moth balls or sprinkled with naphthalene, becomes impregnated with the vapour, creating an atmosphere that moths cannot tolerate.

Any odorous solid sublimes to a considerable extent. The odour is produced by the molecules that escape from the substance and reach our organs of smell. More common, however, are substances which sublime to a negligible degree, sometimes to a degree that cannot be detected even by most elaborate investigation. But, in principle, any solid substance (and we mean any, even iron or copper) evaporates. If we cannot detect sublimation, it only

indicates that the density of the saturated vapour is simply too low to be measured.

This last circumstance is quite natural. The molecules of a solid are bonded together much more strongly than are the molecules of a gas. Moreover, the motions of the molecules in a solid are very ordered, and there is much less opportunity for some chance occurrence that can tear a molecule away from the surface of the solid.

The density of the saturated vapour, in equilibrium with a solid, also increases with the temperature. This is proved by the fact that many substances with a pungent smell at room temperature become almost odourless at sufficiently low temperature.

We cannot substantially increase the density of the saturated vapour of most solids for a simple reason: the substance melts before we make any progress.

If a solid substance can evaporate, the reverse phenomenon must also exist, namely, the conversion of vapour into a solid body, i.e. into a crystal.

The production of crystals from vapours is often employed as a technique for obtaining highly pure crystals. This can be done, for instance, by having the vapour condense on slightly cooled glass.

2. Water Is the Exception to the Rule

The transition from the liquid to the solid state (crystallization) or the reverse transition (melting) consists in a more fundamental rearrangement of the particles. Long-range order in the arrangement of molecules or atoms disappears in melting. At a given pressure, melting always occurs at a strictly definite temperature, called the melting point. At this point, the vibrations of the atoms or molecules become so great that it is no longer possible to maintain long-range order.

If we stop adding heat at the melting point, the liquid and the crystal can be in a state of equilibrium, exactly as when we have a liquid and saturated vapour. The crystal will neither grow nor melt. An example of this equilibrium is ice floating in water. If the temperature is maintained at 0°C , the ice and water can be amiable neighbours as long as we please.

External pressure changes the melting point. As a rule, the melting temperature increases with the pressure, i.e. it is more difficult to melt the substance. There are, however, a few exceptions to this general rule. Ice is one of them. Ice melts more easily at increased pressure. This strange behaviour of ice is due to

another of its anomalies: ice is lighter than water, while the great majority of solids are denser than their liquids. Since pressure compresses the ice and thereby increases its density, it should evidently facilitate melting.

The anomalies of water play a crucial role in our life. Just imagine that water suddenly decided to behave like other liquids. First of all, rivers would freeze to the bottom because ice would sink in water. The very existence of rivers would be threatened. Many rivers have their source in glaciers located high in the mountains. The high pressure due to the masses of ice and snow in a glacier leads to melting in the lower layers of ice. If water behaved normally, as most other substances do, there would be no mountain streams and rivers that they form.

The anomaly of ice is a result of its structure. The ice crystals do not obey the law of close packing of particles. This is why the violation of long-range order increases the density instead of reducing it (as in most substances).

Let us return to Fig. 20. The wide channels in the ice can accommodate, after being slightly expanded, water molecules. As ice melts, molecules "drop" into these channels. Such being the case, the density will, of course, increase.

Hence, we have established that for each substance we can specify characteristic temperatures (at each pressure) at which the liquid and its vapour, the liquid and its crystals, and the vapour and its crystals are in equilibrium.

It remains to answer one question. Is there a point at which all three phases, i.e. three states of matter — liquid, gaseous and crystalline — are in equilibrium? Yes, such a point exists and is unique. It is called the triple point. If water in which ice floats is put into a closed vessel at zero degrees, water vapour (and "ice" vapour) is formed in the free space above the water. At a pressure of 4.6 mm of mercury column, evaporation ceases and the vapour becomes saturated. Now all three phases — ice, water and vapour — are in a state of equilibrium. These are the conditions for the triple point of water.

All substances have such a triple point. Bodies which sublime to only a negligible degree have their triple point at a pressure practically equal to zero.

3. How Crystals Grow

Crystals grow from a melt; they can also be obtained from vapour. It is simplest, however, to observe the growth of crystals from solutions.

Start by dissolving common salt or sugar in water. You will not be able to dissolve as much as you like. At room temperature (20°C), you can dissolve up to 70 grams of salt in a thick glass (holding about 200 grams of water). If you keep adding salt, it will not dissolve, but will settle to the bottom in the form of a residue. A solution which can dissolve no more solute (as it is called) is said to be saturated with the given substance. We use this word in the same sense as in describing the equilibrium between a liquid and its vapour. If we change the temperature, the solubility of the solute in the solvent is changed as well. Everybody knows that hot water dissolves most substances more readily than cold water.

Imagine now that you have prepared a saturated solution, say, of sugar, at a temperature of 30°C and cool it to 20°C . At 30°C you can dissolve 223 grams of sugar in 100 grams of water, and at 20°C , only 205 grams. Then, in cooling from 30° to 20°C , 18 grams of sugar turn out to be "redundant" and, as they say, are precipitated from the solution. Hence, another way to obtain crystals is to cool a saturated solution.

We can do the same thing in a different way. Prepare a saturated solution of salt and let it stand in an open glass. After some time has passed you find crystals of salt on the bottom. Why did they form? Look at the glass again, more carefully, and you can see that another change occurred together with the appearance of crystals: there is less water. The water evaporated and left "redundant" matter in the solution. Thus, still another way to form crystals is to evaporate the solution.

How are crystals formed in a solution? We have mentioned that the crystals precipitate from the solution. Does this mean that no crystal was observed for a whole week and then, in a flash, it appears as if by magic? No, this is not so; crystals grow.

You cannot, of course, observe the initial instant of growth with the naked eye. First, a few of the randomly moving molecules or atoms of the dissolved substance (solute) assemble by chance in approximately the order which is required to form the crystal lattice. Such a group of atoms or molecules is called a nucleus.

Experiments show that nuclei are more frequently formed when the solution contains extremely fine particles — dust specks — of some foreign substance. Crystallization proceeds at a higher rate and more easily if a tiny seed crystal is put into the saturated solution. Then the precipitation of the solid substance from the

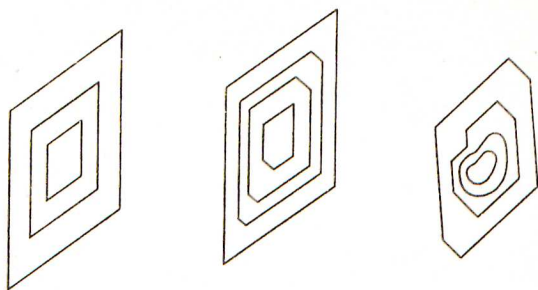


Fig. 64. At the left: crystal growth where the number of faces remains constant; in middle: in the course of growth, fast-growing faces of the crystal may disappear and new faces may appear; at the right: a shapeless fragmentary crystal acquires regular shape during growth.

solution consists in the growth of the seed crystal rather than in the formation of new small crystals, i.e. nucleation.

The growth of a nucleus does not, of course, differ in any way from the growth of a seed crystal. The advantage of using a seed crystal is that it "draws" to itself the substance separating out of the solution, hindering, in this way, the formation of a large number of nuclei. If a great many nuclei are formed at once, they hinder each other in growing and we cannot obtain large crystals.

How do new portions of atoms or molecules, separating out of the solution, arrange themselves on the surfaces of the nucleus?

It has been found that the growth of a nucleus or seed crystal consists in the seemingly outward motion of its faces in a direction perpendicular to each face so that they remain parallel to their initial positions (the crystal seems to expand). Naturally, the angles between the faces remain constant. The constancy of these angles is one of the vital features of crystals and is due to their lattice structure.

The successive outlines of three growing crystals of the same substance are shown in Fig. 64*. This is what we can observe under a microscope. In the case of the crystal shown at the left the number of faces remains constant during growth. The middle

* This illustration has been taken from a book called *The Formation of Crystals* (in Russian), which was written by A. V. Shubnikov, to whom we are indebted for his detailed research in the growth of crystals.

crystal is an example of how a new face appears during growth (at the upper right) and subsequently disappears.

It is important to note that the rate of growth of the faces, i.e. the velocity at which the faces seem to move while remaining parallel to their initial positions, is not the same for various faces. We also find that the faces which disappear are those that grow fastest, for instance, the lower left face in the middle crystal. The slowest-growing faces, on the contrary, become the widest, or, as we say, best developed, ones. It is a principle that a grown crystal is always bounded by its slowest-growing faces.

This is especially clear from the illustration at the right of Fig. 64. Here a formless fragment acquires the same shape as the other crystals, precisely owing to anisotropy of growth rates. Quite definite faces develop at the expense of others more and more resolutely and impart the shape to the crystal that is inherent in all specimens of this substance. The characteristic shape of a crystal is called its "habit".

These features of growth are typical for all kinds of crystallization, whether from a solution, a melt or a vapour. The seemingly parallel motion of the faces suggests that the substance separating out is deposited on the face in layers, and that a succeeding layer is not started until the preceding one is completed.

Shown in Fig. 65 is an "incomplete" packing arrangement of atoms. In which of the positions indicated by letters is a new atom, attaching itself to the crystal, most likely to remain secured? Without doubt, in position *K* because here it is subject to attraction by its neighbours from three sides. In position *L* the new atom is attracted from two sides and in position *M*, from only one.

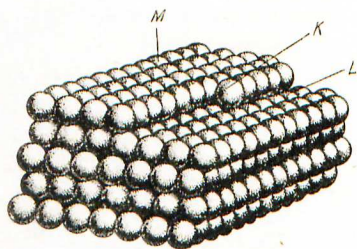


Fig. 65. The growth of a monoatomic crystal shown schematically. The next atom added to the crystal will most likely try to get into the position marked by letter *K*; position *M* is least "attractive". This scheme shows how crystals grow by layers.

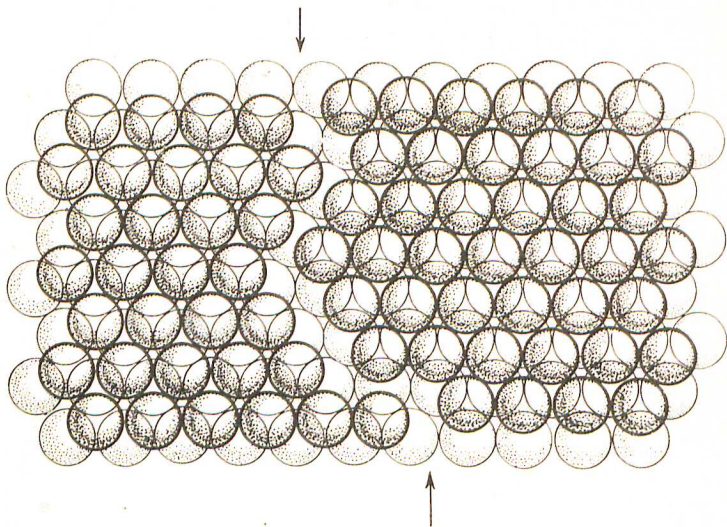


Fig. 66. After the previous layer of the crystal was completed, two new atoms were accidentally attracted and attached above two hollows of the layer. A new layer began to grow about each atom. Thus two sections of the layer appeared with a distortion in the stacking arrangement of the atoms at the boundary between the sections.

This is why a row is first completed, then a whole layer and finally a new layer.

Crystals ordinarily grow in this way. But imagine that by chance a layer begins to grow from several places at the same time. You remember that in the close packing arrangements of spheres, the sphere of the next layer may occupy two different kinds of hollows. If the preceding layer is of type A, the next layer may be of either type B or type C. Hence, in the growth of the layer, a new layer may originate from several points at the same time and may consist of several regular portions, some of the B and the rest of the C type (Fig. 66). At their boundaries, the portions of different types do not fit together and we find defects in structure.

If subsequent layers also grow with defects, we have three-dimensional islands with regular packing arrangement instead of plane ones. Defects are found at the boundaries of these islands. In the piecewise structure of a body described above, there may be "coarser" defects than those occurring in laying down layers.

At the boundaries between the pieces there may be portions with inaccurate lattice constants and lower density.

If crystallization takes place at a low rate, structures with defects (in any case, of the last kind mentioned above) are formed much less frequently. Each atom added to the crystal has sufficient time to find its proper place. Irregular structures appear in rapid crystallization.

The formation of three-dimensional portions of regular sphere-type close packing, just described, was observed in the crystallization of cadmium iodide. The close packing arrangement concerns the atoms of iodine; the small cadmium atoms occupy the voids (interstices) between the close-packed iodine atoms. Two kinds of defects are possible in the structure of such crystals: defects in the formation of the close packing of the iodine atoms and defects in filling the voids with cadmium atoms. Evidently, both kinds of defects are found in nature.

4. Spiral Growth

The picture of crystal growth described above is not always quite correct. Actually, it is much more complicated. Calculations show that an atom is particularly reluctant to occupy a position of the *M* type (Fig. 65). When an atomic plane is completely built up and a new plane is to be filled with atoms, the formation of a new layer is an event of low probability. Such growth can feasibly occur only when the degree of supersaturation of the substance surrounding the crystalline nucleus is considerable.

In 1931, however, it was established that crystals have a fairly high rate of growth even at negligible degrees of supersaturation. The growth observed in experiments is 10^{1000} times as intensive as that predicted by calculations. There is probably no other case in physics when theory and experiment disagree so greatly.

What makes it so easy for each new layer to start growing on a crystal? This question puzzled physicists for many years. The answer was found only in 1945. Attentive observations and much brainwork finally led to the solution. Easy crystal growth was found to be possible when there are screw dislocations in the crystal on which growth occurs.

The presence of such a dislocation enables the crystal to grow continuously by the addition of atoms that occupy a position of type *K*. How is this possible? A crystal with a screw dislocation is shown in Fig. 67a. The shaded edge of the step is very convenient for adding new atoms. During growth, the

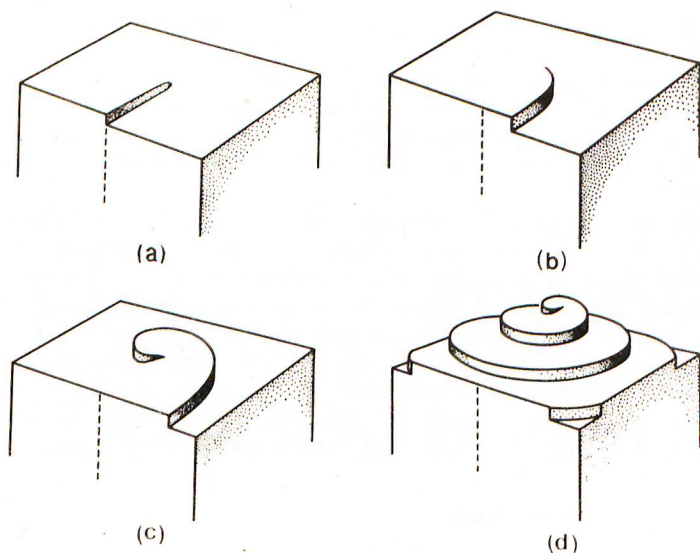


Fig. 67. Growth of a crystal having a screw dislocation. The consecutive stages of growth illustrate the formation of a winding staircase.

surface of the crystal attracts atoms of the liquid or vapour to itself. The atoms “run” along the surface “looking” for a place to attach themselves. The only suitable place is at the edge of the step. Atoms add continuously at this edge which begins to move along the face of the crystal.

The most interesting feature is that this motion (growth) of the edge and step is not in a direction which maintains the edge parallel to its initial position. The end of the edge, at the axis of the screw dislocation, remains stationary (at this end, the edge tapers down and there is no place for the atoms to become attached). Hence, willingly or unwillingly, the edge of the step begins to bend and gradually becomes a spiral strip. Here again we find the winding stair feature inherent in screw dislocations. The crystal can continue to grow in this manner for an unlimited length of time, building up the face in the form of a spiral turret. The central part leads and seems to pull along all the other steps of the spiral. The lower steps are built outward consecutively to the edges of the face on the crystal.

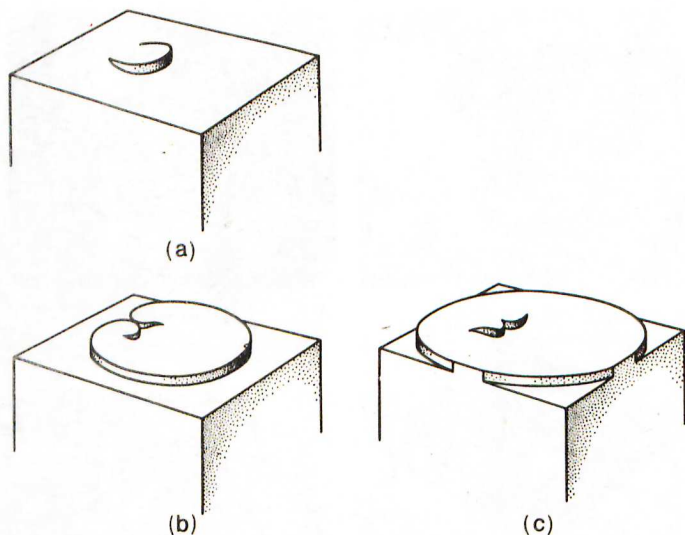


Fig. 68. Growth of a crystal having two opposite (right- and left-hand) screw dislocations. The consecutive stages of growth are shown.

A turret of different design is obtained when there are two opposite (left- and right-hand) screw dislocations close to each other. This kind of crystal growth is shown schematically in Fig. 68. Note that two screw dislocations do not produce a spiral staircase. The turret consists of completed platforms in terraced steps. As the crystal grows each platform spreads out to the edge of the crystal face, and new platforms are continually formed at the top.

All diagrams and diagrams, the reader may object. Can we believe in such diagrams, like the ones drawn in Fig. 69? But here the reader is mistaken: these are not diagrams, they are photographs of real crystals. Investigations have brilliantly confirmed the dislocation theory of crystal growth.

Many crystals grow in rounded spirals or platforms. This happens when all directions of growth on the face of the crystal are equally possible.

This situation, however, is not necessarily true for a crystal. On the contrary, it is more natural to suppose that a crystal grows in rows.

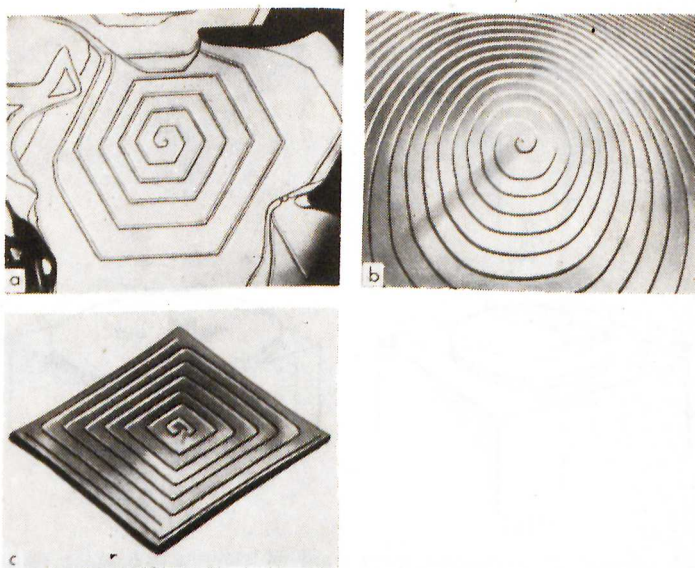


Fig. 69. Pictures of crystals grown by the methods illustrated in Figs. 67 and 68. (a) Surface of a silicon carbide crystal. (b) Spiral layer formation photographed with oblique illumination (silicon carbide). (c) Crystal of stearic acid with layer growth originating from a pair of opposite (right- and left-hand) screw dislocations.

Spiral growth with rows of atoms is excellently illustrated by four successive photographs of the growing face on a crystal of cadmium iodide (Fig. 70). We have no difficulty in guessing that we are dealing with the growth of a plane with a closest packing arrangement of spheres.

The four photographs in Fig. 70 are also appropriate in that they clearly demonstrate how the top of the spiral grows. The central dash in the photograph is the region of the screw dislocation. The numbers indicate the growing rows of atoms.

The height of the step of the spiral can be precisely measured. In complete agreement with theory, this height is found to be equal to or a multiple of the lattice constant of the crystal in the direction perpendicular to the plane (face) on which growth takes place. A single dislocation corresponds to a step height equal to one lattice constant. Sometimes quite high steps

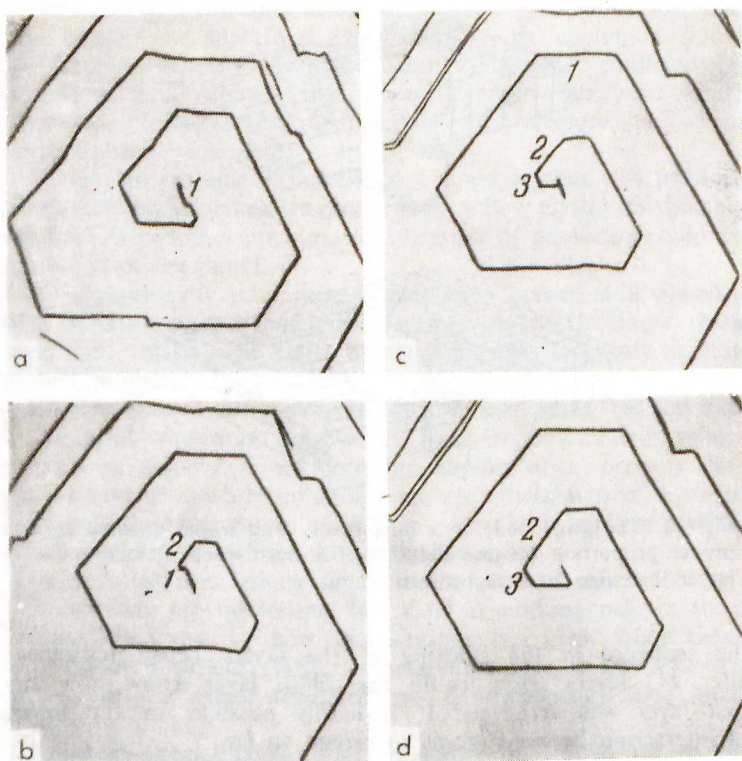


Fig. 70. Photographs illustrating spiral growth of a crystal of cadmium iodide.

are observed. This means that several dislocations of the same hand have met in the crystal.

On page 128 we discussed the structure of crystals with defects in the stacking of the layers. We can readily picture a regular crystal with its layers stacked according to the arrangement ...ABAB... or ...ABCABC... . We can also readily agree that a structure with disordered stacking of the layers can easily occur. But one feature of stacking arrangements seemed to be an incomprehensible puzzle. There are crystals in which the pattern of successive layers extends over a great number of layers before it is repeated, sometimes over 10 or even 20 layers. Specimens of silicon carbide have been found in which

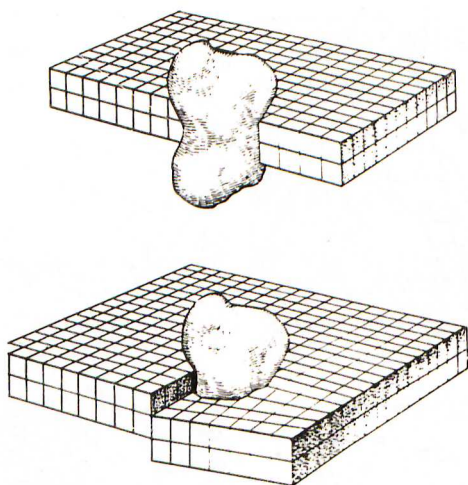


Fig. 71. The large body is a dust speck. The whole drawing is in proper proportion because the size of a dust speck is many times larger than the distances between atoms.

the sequence in the stacking of the layers began to repeat after 243 layers. How could the 244th layer know how the first layer was arranged? It is hardly possible for the forces of interaction between atoms to extend so far.

The spiral growth of crystals provides the way out of our predicament. A series of screw dislocations can lead to the formation of a step many layers high. This step becomes the period of repetition of the structure.

Dislocations govern crystal growth and, at the same time, are formed in the growth process.

Evidently, one of the possible ways in which a dislocation can be formed is the entrapping of a foreign particle, for instance, a dust speck, during crystal growth. This is illustrated in Fig. 71.

5. Crystal-Crystal Transformations

We know that the same substance can produce crystals of entirely different structures. Examples were given earlier in the book (grey and white tin, red and yellow sulphur, two kinds of iron, graphite and diamond, and many others).

How are the different kinds of crystals produced; how can you obtain one kind and how another? By cooling a liquid we force it to crystallize; by making a vapour condense on a cold backing we can also obtain crystals. But what kind? This was found to depend upon the pressure at which crystallization takes place.

Here is an example. When we cool liquid sulphur at a pressure above 1288 atmospheres, we obtain small yellow crystals of rhombic sulphur. At ordinary pressures, red crystals of monoclinic sulphur grow out of the liquid.

An exceptionally interesting phenomenon occurs at a pressure of 1288 atmospheres and a temperature of 151°C . Under these conditions, crystals of both kinds grow simultaneously in the molten sulphur.

In exactly the same way, we can obtain small red crystals if we cool vaporous sulphur at high pressures, and yellow crystals of sulphur if we cool the vapour at a pressure less than 1 mm of mercury column. Here also there is only a single point – at the temperature of 95.5°C – when both kinds of crystals grow simultaneously from the sulphur vapour.

Other substances behave in about the same manner.

These facts are interesting, but there is nothing new in them for us. We know by now that crystals can grow from either a liquid or a vapour. What is remarkable here is that different crystals of the same substance can be transformed into each other.

However, special conditions are needed for white tin to be transformed into the grey kind, yellow sulphur into the red form and for similar transitions of other substances. In this respect, these phenomena fully resemble melting. For red sulphur to transform into the yellow kind at standard pressure, the temperature must be below 100°C . Above this temperature and up to the melting point, the stable order in the arrangement of the atoms is that found in red sulphur. As the temperature drops, the vibrations of the atoms are reduced and, beginning with 110°C , nature finds a more convenient arrangement of the sulphur atoms. A crystal-crystal transformation occurs.

Each of the crystalline phases has its region of stable states, determined by the ranges of pressure and temperature. The laws governing the transformation of one crystalline form into another are the same as the laws governing melting and evaporation.

For each pressure, the temperature can be indicated at which both kinds of crystals peacefully coexist. When we raise the

temperature, the crystals of one kind are transformed into the other kind. When we lower the temperature the reverse transformation takes place.

True, a relevant point that can be made here is that in transformations in the solid state, the transformation may in some cases proceed readily only in one direction. Carbon can serve as an example: diamond can be easily converted into graphite; the reverse transformation was considered impossible until recently. The conditions required for such a transformation are now known, though it is not easy to accomplish.

Transformations in the solid phase are transitions of one long-range order into another, also long-range, order. The mechanism of such transformations is of especial interest.

The rearrangement of the atoms from one kind of order in their positions to another must take place so that the atoms are displaced over minimal possible distances and travel from their previous positions to the new ones in the easiest way.

When an officer commands "Form fours!", the soldiers change the order of their files, making the minimum number of necessary motions. In this sense, there is much in common between changes of marching formation and the transformation of one solid phase to another.

But examples are more visual than words. Solid phase transformations of elements are simplest when the structures of both phases are of the type represented by the close-packed arrangement of spheres.

For example, both cobalt and thallium may have the packing arrangement ...ABCABC... (face-centred cubic lattice) as well as the arrangement ...ABABAB... (hexagonal closest-packed lattice). How is one packing arrangement transformed into the other? Figure 72 again depicts the features of packing arrangements of spheres that we are now familiar with. (It is a projection of the structure onto the plane of the drawing.) A close packing arrangement of spheres is made up of layers. All possible stacking arrangements of the layers of any of the innumerable packing arrangements of spheres (see page 80) one on top of another, can be reduced to three stacking arrangements, denoted in Fig. 72 by x's, small circles and small squares (A, B and C). The x's are the first story, circles are the second and squares are the third.

In the arrangement ...ABCABC..., the stacking sequence is repeated after each three layers; in the arrangement ...ABABAB..., after each two layers. The latter is a two-story stacking arrangement. Consequently, in Fig. 72, either the circles or the squares must

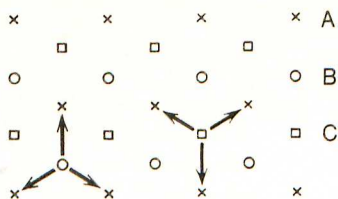


Fig. 72. Diagram of the transformation of the closest packing arrangement ...ABCABC... into packing arrangement ...ABABAB.... The three stories of atomic stacking arrangement are indicated by three different symbols.

be eliminated. Three- and two-layer structures differ basically; how do we go over from the former to the latter?

Arrows are shown in Fig. 72. It is evident that if we move a layer of circles or squares in one of these directions, we can transfer layer A to layer B or C, layer B to layer A or C, or layer C to layer A or B. Figure 72 illustrates the rearrangement of a three-story structure into a two-story one according to the scheme

...AB CA BC AB CA BC...

...AB AB AB AB AB AB...



The positions of the letters show that of six layers two can remain in their previous positions, and four layers must be displaced to convert C into A, A into B, B into A, and C into B.

There are, of course, many ways to displace these layers in various possible directions that solve our problem.

The displacement of a layer along another layer requires work. The easiest transformation would be one in which four layers ...CABC... could be transferred to the position ...ABAB... in a single displacement. It is clear, however, from the directions of the arrows in Fig. 72 that this is impossible. Still, we can economize on the work required for displacement if we transfer the layers in pairs. Look again at Fig. 72. Three arrows pointing from squares C show three directions in which displacement of two adjacent layers ...CA... converts them into layers ...AB... (the squares become x's, and the x's of the neighbouring layer become circles).

Three arrows (pointing in the opposite direction with respect

to the first three) from the circles (layer B) indicate three directions in which the displacement of two adjacent layers ...BC... converts them into ...AB... Lay a piece of tracing paper on Fig. 72 and make this displacement. You will see that I am right.

Hence, each six layers requires two displacements in order to transform stacking arrangement ...ABCABC... into arrangement ...ABABAB... Moreover, each of the "displacements" can be accomplished in any one of three directions.

In transformations of this type, it was even found possible to grow a single crystal of the phase ...ABAB... from one crystal of the cubic-lattice phase. Ordinarily, this cannot be done. The growth of crystals of the new phase begins simultaneously from many centres of nucleation (the monocrystal is converted into a finely crystalline substance). More frequently, the crystal disintegrates in the transformation. Sometimes the external "shell" is retained and the finely crystalline substance occupies the strictly regular symmetrical volume of the polyhedron, the habit of the former monocrystal.

The cause of these difficulties is known. The crystals of the new phase can begin to grow from various places. But in the face-centred cubic packing arrangement we can have four different systems of closest stacked layers. Return to Fig. 13. In the lattice shown at the left, the densest layers are perpendicular to the body diagonals of which there are only four (a cube has eight corners). Hence, from a crystal with the stacking arrangement ...ABCABC..., crystals of the ...ABABAB... type can grow with four different orientations.

However, the transformations of cobalt and thallium from the stacking arrangement ...ABABAB... must have the following feature: however the displacements of the atomic layers may occur, they must produce a new crystal with the same orientation.

In transformations of the packing arrangement of cobalt atoms ...ABABAB..., an unoriented finely crystalline substance can never be produced. Most likely, the transformation leads to a crystal with defects in the stacking of the layers, i. e., to a stacking arrangement

...ABCABCABCACABCABCABABCABCAB...

The study of the rearrangement of atoms in phase transitions began with investigations of iron and steel. At high temperatures iron exists in the form of a close-packed atomic arrangement according to the sequence ...ABCABC... (face-centred cubic lattice). At low temperatures the iron atoms occupy the sites of a body-centred cubic lattice.

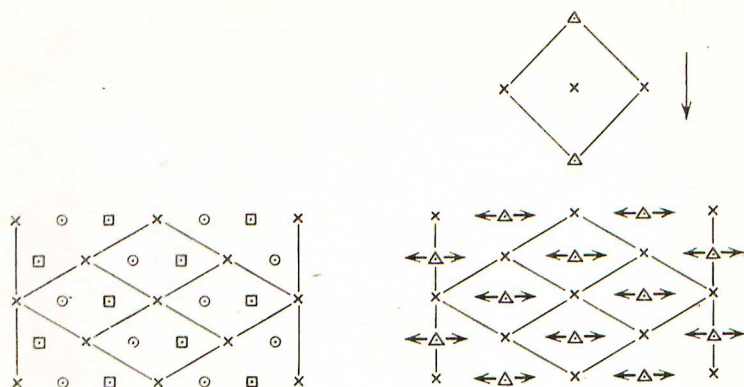


Fig. 73. Transformations of iron. The closest packing arrangement corresponds to the crystalline state of iron stable at high temperatures (at left). Shown at the right is a body-centred cube (compare with Fig. 16), projected along a diagonal of a face on the cube.

This transformation is of fundamental significance in metallurgy and deserves more detailed treatment.

What happens when the temperature is raised? The answer can be found in the diagrams shown in Fig. 73. Shown again at the left is a close stacking arrangement according to the sequence ...ABCABC..., and at the right, a body-centred packing arrangement, depicted in a somewhat unusual way. It shows the projection of the arrangement of the atoms as we would see it if we looked along a diagonal of a face on the cube.

There does not seem to be much in common between the two drawings. The left-hand structure is three-storied, the right-hand one is two-storied (the little triangles represent the second story). This is the main difference. Another, less significant difference is in the angles of the rhombuses (not shown in the drawings).

As the iron is heated, the vibrations of the atoms increase and, at temperature of 906°C , the less dense body-centred packing arrangement becomes disadvantageous. The two-storied structure is changed into a three-storied one by alternate displacements of the layers denoted by little triangles. The odd layers, for instance, are moved to the left and the even ones, to the right. These displacements take place along a diagonal of the rhombus, whose angles are changed at the same time.

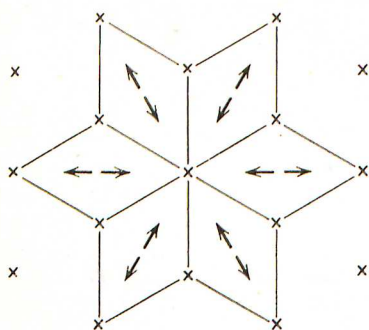


Fig. 74. Possible orientations in crystal growth of body-centred cubic iron (stable at low temperatures).

In contrast to cobalt transformations, it is hardly possible for a single crystal of iron of one phase to be transformed into a single crystal of the other phase. It is evident that in a phase transition of iron, the small crystals of the new phase may be differently oriented. In cooling a single crystal of iron, small crystals of the new phase begin to grow from the transformation point in 24 different directions. The figure 24 is obtained as follows. A face-centred cubic crystal lattice has four densest planes. Return to Fig. 13 again. In such a crystal, the densest planes are perpendicular to the body diagonals, of which there are four.

Since the transformation begins at different points in the substance, independent of one another, any of these densest layers may begin rearrangement. The crystals of the new phase may begin growing in the densest layer with six different orientations, as is clear from Fig. 74. Well, and $4 \times 6 = 24$. Observations of this type led to an understanding of the nature of the displacements that rearrange the order of the iron atoms.

In expounding laws of nature, we can profit from a great deal of attention paid to a special example in two cases. First, when the example is typical, and secondly, when we are dealing with an outstanding exception to the rule. We have given two examples of oriented transformations. In such processes, the rearrangement of the atoms proceeds in such a manner that the various atoms repeat one another's motions exactly like soldiers do when they obey a command of their officer to change their marching formation.

What, then, is this: a rule or an interesting exception? When the author prepared the preceding edition of this book, he thought that he was presenting typical examples. Recent investigations,

however, have almost upset this point of view, which is still widely held.

As mentioned above, only rarely can a monocrystal be grown from a monocrystal. Crystals often disintegrate in transformations. This circumstance did not permit extensive experiments to be conducted to check the basic proposition: how often do the two phases, parent and daughter, coincide in orientation? If they do coincide, this is a proof of the oriented, ordered transformation of one crystal into the other. But what if they do not?

In his laboratory the author conducted experiments whose aim was to learn to grow monocrystals of one phase out of monocrystals of another phase. The items experimented on were various organic substances. To ensure "mild" conditions for the transformation, the crystal was put into a drop of glycerin or some other similar substance. Such a liquid evidently provides suitable protection for the crystal. Using this technique, it was found possible to grow a crystal within a crystal. More than that; we learned to "drive" the transformation in either direction. By raising or lowering the temperature, the faceted boundary between the phases, so clearly visible in Fig. 75, can be made to move in one or the other direction.

Having such items available, we could investigate the central problem with complete assurance, employing many physical methods. This problem is: Does any regular relationship exist between the orientations of the phase? The answer was found by experiments and is as follows. The lattice of one substance may be oriented in many cases entirely by chance with respect to the lattice of the other substance. If there is no regular relationship, there can be no oriented growth. It turns out that in its growth one crystal uses the other crystal as a homogeneous medium. In short, the growth of a crystal from a crystal in such cases in no way differs from the growth of a crystal from a liquid.

How can we visualize the formation of a nucleus of the new phase and its growth under the extremely crowded conditions and low mobility of the atoms in a solid? But, in the first place, opportunities for the motion of atoms and even molecules in solids are not so meager, as we shall see a few pages further on. In the second place, there are many places in the crystal where atoms and molecules can easily pass each other. As we know, there are many voids, cracks and dislocations in crystals. We can contend that the growth of the new phase begins precisely at such places. Only a little free space is required for a molecule to separate itself from the old phase, shift over

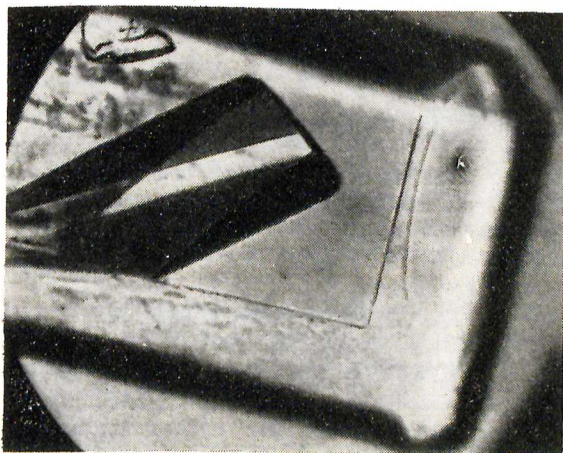
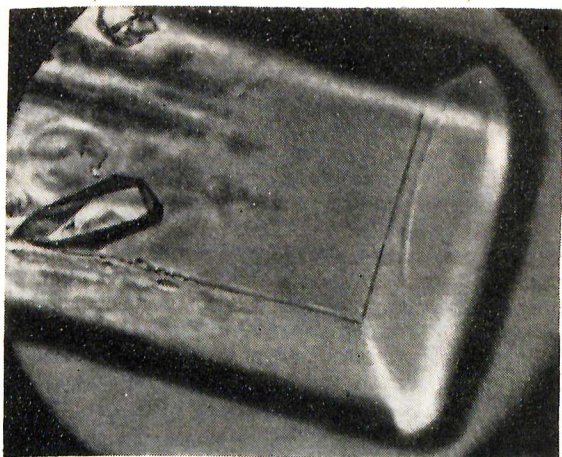


Fig. 75. Growth of a crystal within a crystal of the organic substance paradichlorobenzene observed under an optical microscope.

a short distance and become attached to a crystal of the new phase in the required position.

It is probable that in most cases the new phase grows out of the old one more or less like a crystal grows from a liquid. When it grows from a liquid, however, nothing hinders the crystal from growing in any direction it likes. This may also be true for the growth of a crystal from a crystal, but only when all directions can be "overcome" with equal ease. Also feasible are intermediate cases when there are many directions, spread like a fan, along which the new nucleus can conveniently grow. On the contrary, there may be practically only a single direction of "easy" growth of the new phase.

Thus we see that we have just as much reason to expect as not to expect the coincidence of orientation in the transformation of one crystalline phase into another.

6. Delays in Transformation

No matter how slowly we heat a solid to the melting point, we cannot "skip" over this point. Ice cannot be preserved at a temperature above zero degrees. There are, however, many cases in which liquids can be supercooled. This sometimes requires no special measures whatsoever. We cool a liquid, the freezing temperature has been left far behind, and the crystals have not the slightest intention of forming. Certain liquids (glycerin) simply become more and more viscous upon being supercooled and exist in such an amorphous state for months and years.

How, then, do we know the "correct" freezing point, or temperature of crystallization? Maybe there are substances that crystallize whenever they want to? No, this is not so. Every liquid has a strictly definite freezing point at a given pressure. To prove this, you must have the substance available in two states, liquid and crystalline.

The truth is revealed when we bring the liquid into contact with a crystal. Then, one of three things may happen: the liquid "devours" (actually melts) the crystal, the liquid and the crystal coexist peacefully, or the crystal begins to grow. The border line is the transformation point.

Thus, if we have a small crystal, we have no trouble finding out whether the liquid is in the supercooled state. We throw the crystal into the liquid; if the liquid is supercooled, crystallization begins immediately. At a high degree of supercooling, the effect is exceptionally violent. If we supercool water and

throw a snow-flake into it, needles of ice spread in all directions at an enormous speed over the water and in an instant the transformation is completed throughout the whole volume.

Of special interest are delays in crystal-crystal transformations. Here we can delay the transformation, so to speak, in either direction. At 95.5°C , yellow sulphur should be transformed into the red kind. If we heat the sulphur rapidly, we can "skip over" this transformation point and bring the sulphur to the melting point (113°C) without any transformation. Next we begin to cool the melt. At 113°C , crystals of red sulphur begin to grow. Further cooling does not initiate the transformation; not only at 95.5°C , but even at room temperature you have the small red crystals at your disposal for a considerable time. Soon, however, you find they have turned into a yellow powder. The transformation is slow but is completed in about twenty-four hours.

Here, as well, the true transformation temperature can most easily be determined by bringing the small crystals into contact with each other. If we press the red and yellow crystals tightly together and maintain a temperature of 96°C , the red crystal "consumes" the yellow one; at 95°C , the yellow crystal "devours" the red one.

We often deal with phases of a substance that are supposed to exist at an entirely different temperature. It may be vital to know whether we have stable crystals. White tin is converted into grey tin when the temperature is lowered to 13°C . But white tin is used in many utensils we commonly employ and we know that nothing happens to it in the winter time. White tin can withstand supercooling by 20 to 30 degrees with no trouble, as a rule, but under conditions of an extremely severe winter, it begins to change into grey tin and disintegrate. This is referred to as "tin plague". It is said that the expedition of Robert Falcon Scott (1868-1912) to the South Pole (1912) perished because they did not know this fact. All of the liquid fuel that the expedition took along was in containers having seams soldered with tin. In the extremely cold antarctic weather, the white tin turned into a grey powder, the seams became unsoldered and all the fuel leaked out.

As with sulphur, white tin can be converted into the grey kind at a temperature slightly below 13°C only if a tiny grain of grey tin gets on the item made of white tin.

To understand the reason why transformations may be delayed, we must first consider the difference between liquid-crystal and

crystal-crystal transformations on the one hand, and crystal-liquid transformations on the other. In the last kind, long-range order in the arrangement of the atoms disappears, and in the first two, it has to be set up anew. Disappearance of long-range order does not require much effort. Melting begins at the surface: atom after atom is detached from its neighbours, dropping out of the strict array.

In crystallization, short-range order develops into long-range order. This process also begins at the surface and must pass into the substance. The atoms are obliged to set up strict order under conditions of an extremely crowded environment. Coordinated movements (speaking of people, we would say "well-planned" movements) are required to set up proper order. Even more difficult is the task of setting up atomic order, which requires, as we have seen, "organized" displacements from certain positions to others.

Solid-state transformations always begin at the grain and block boundaries, at dislocations, in voids, in short, wherever some free space is available. The first step is of prime importance; the saying "Well begun is half done!" is an excellent illustration of such processes. If even only several dozens of atoms get into the positions corresponding to the new order, oriented growth of the nucleus begins. One after another atoms go over from the previous, less convenient order or from disorder (in crystallization) and join the growing nucleus.

The action of a small seed crystal, which eliminates supercooling, has the same guiding function.

7. Particles Change Places

Recent experiments indicate that the potentialities for displacement of the particles of a solid, either atoms or molecules, have hitherto been underrated to a considerable extent. Of course, and this is one of the basic features of solids, the atoms or molecules mainly vibrate about their equilibrium positions. However, an atom of a crystal can leave its equilibrium position and is capable, by shoving its way between its less vigorous neighbours, to move around in the crystal lattice.

If this phenomenon did not exist, diffusion of atoms in a solid would be impossible. In its physical sense, diffusion can be approximately defined as infiltration or penetration. The diffusion of foreign atoms in a solid body has long been known to physicists.

The surface layer of steel can be impregnated with carbon (in carburizing for casehardening), nitrogen (nitriding) or boron.

But not only foreign atoms can move about in a crystal. Atoms of iron can roam about in an iron crystal; atoms of copper in copper, etc.

Until recently, this phenomenon was a mere supposition, unsupported by fact. It is easy to observe the diffusion of carbon in steel. You can look at the specimen under a microscope or make a chemical analysis (or you can investigate any physical properties, which change, of course, when foreign atoms penetrate into the crystal). Diffusion proceeds to a great depth and can be revealed without taking much trouble. At a temperature of 200° to 300°C , silver impregnates lead in appreciable amounts at a rate of several centimetres per hour. But how can we observe the diffusion of iron into iron or copper into copper? This can be done with the aid of tagged, or labeled, atoms, also called tracers. Employing modern nuclear reactors we can make any substance radioactive. All that is required is to put the substance into the nuclear reactor for a certain length of time. The neutrons produced in the reactor make the atoms of the substance radioactive.

Radioactive substances emit penetrating radiation which can be measured by instruments of exceptionally high sensitivity. When a piece of radioactive copper is pressed tightly to a piece of ordinary copper, the latter, after a short time, also becomes radioactive. This proves, beyond the shadow of a doubt, that tracers have penetrated it.

Tagged atom techniques enable the diffusion of "domestic" atoms to be studied with the same ease as that of foreign atoms.

It is not so easy to explain the travelling of an atom through a crystal lattice constructed in accordance with the close-packing principle. If the atoms of a crystal were at rest, diffusion would be a completely inexplicable phenomenon. But we know that the atoms vibrate in a crystal. At the instant one atom moves away from its equilibrium position, the neighbouring atom can jump into its place. The returning atom can do nothing but occupy the place of its more "nimble" neighbour. This is how atoms change places. Such an exchange is not easy to accomplish, of course, if only two atoms participate in it. It is just as difficult to make your way to the front of an overcrowded streetcar if only the passenger immediately in front of you tries to make room to let you pass. If, however, a group of passengers, standing

in front of you and at the sides, respond to your request to let you pass, each one will have to stand just a little closer to his neighbours and you will have no trouble in exchanging places with the people in front of you.

This is probably what happens when diffusion of atoms in a solid occurs: a whole group of atoms participates when two atoms change places. An atom slips ahead only when the thermal vibrations of many atoms accidentally create a favourable situation for such exchanges.

There is no doubt that all kinds of dislocations, voids and fissures, always available in a crystal, play a tremendous role in diffusion phenomena. The presence of a vacant site helps the atom to move along, step by step, through the lattice, "pushing aside" atoms that hinder its progress into these voids.

When a foreign atom is much smaller than the host atoms, it can move along the lattice without changing places with other atoms. After waiting for favourable conditions, such an atom can slip from one interstice of close-packed spheres into the neighbouring interstice.

Diffusion is a counter effect. When we press a plate of zinc to a plate of copper, zinc atoms impregnate the copper and copper atoms impregnate the zinc. True, the rates of these counterflows may differ greatly.

The diffusion of atoms through a crystal depends upon many factors. Of interest is the following. The diffusion rate is highest when the travelling atom in no respect resembles the host atoms of the crystal through which it passes. The "xenophobic" atoms of the crystal make every effort to get rid of the stranger who does not look like them, sending him on his way as soon as possible. The lowest rate is observed for atoms in their own crystal and in a crystal of atoms from the same column in Mendeleev's periodic table.

As we mentioned before, fissures and distortions of the crystal lattice facilitate diffusion. This makes it clear why the "travelling" of foreign atoms is much faster in a deformed metal.

Diffusion of atoms is a phenomenon that has been known to investigators for a long time, but the possibility of progressive motion of giant molecules through a crystal is a recent discovery.

Employing a particularly interesting technique (known as the nuclear magnetic resonance method), physicists were able to show that as the temperature is raised, molecules change over from vibratory motions to a much freer way of life. First one, then another molecule turns into an improper position or even leaves

its site in the crystal, moves through a fissure and, with a different orientation, finds a new nook in the crystal.

It is probable that defects in a crystal play a basic part in the diffusion of molecules. But still, strange as it may seem, the process in which large molecules advance by changing places with neighbouring molecules occurs in a perfect crystal as well.

In one way or another, particles of a crystal possess ample opportunities for various kinds of movement. Consequently, the numerous transformations in a solid — the crystal-crystal transformations just discussed and an extensive class of chemical reactions that occur in solids — should not be very surprising.

Of course, particles do not roam about in a crystal because they have the wanderlust. They are simply obeying the laws of physics.

What, then, are these laws and regulations that compel atoms and molecules to travel under such adverse conditions? You will find the answer in the next chapter.

Order or Disorder

1. Probability and Disorder

When molecules are not subject to external forces and when there are practically no cohesive forces between them, their arrangement attains complete disorder. To get rid of the cohesive forces, the body must be heated, melted and evaporated. It is more of a problem to get rid of the external forces, primarily of the force of gravity. The influence of gravity has no appreciable effect, however, on a layer of gas that is thin in the vertical direction. In this layer the gas molecules are in perfect disorder.

Try to answer the following: Why does a disordered arrangement of molecules with uniform density emerge when the molecules are moving in an entirely random fashion?

We shall begin by solving the problem of accommodating six different animals in three pens so that each pen has two lodgers. Our animals include a dog, a cat, a hare, a rabbit, a fox and a hedgehog.

We begin by settling the first two tenants in the first pen. This can be done in various ways: we can move the dog in with the cat, the dog with the hare, ..., the cat with the hare, the cat with the rabbit, etc. Count all the possible combinations; you will find there are fifteen. After filling the first pen, the lodgers of the second must be selected from the four remaining animals. If, for instance, the first pen is occupied by the cat and dog, the second pen can accommodate the hare with the rabbit, hare with the fox, hare with the hedgehog, rabbit with the fox, rabbit with the hedgehog and the fox with the hedgehog. Six possible combinations in all. Evidently, all the possible combinations of accommodating all our animals in the pens equal 6×15 , i. e. 90.

Hence, there are as many as 90 ways of uniformly distributing only six animals in three pens.

How many ways, then, are there for uniformly distributing 1000 animals among 100 pens? A thousand, ten thousand or a

hundred thousand? Calculations show that this number is approximately equal to one followed by a thousand zeros.

We can readily understand that when we are dealing with gas molecules, of which there are a million million millions in a single cubic centimetre, the number of different ways to achieve their macroscopically uniform distribution throughout the volume is inconceivably immense.

At the same time, the number of ways in which we can achieve macroscopically nonuniform, more or less ordered distribution of the molecules is considerably less. The greater the deviation from uniform ideal disordered distribution, the less this number will be.

If we alter the conditions in our example with the animals to a distribution between only two pens with one animal in each, we can easily figure out that there are only 16 different ways (instead of 90) to get our job done. The number of ways to distribute 1000 different animals among 100 pens so that the first pen contains 901 animals and the rest of the pens, one each, is a figure in which one is followed by only hundreds instead of thousands of zeros.

When we deal with a million million million molecules, the difference between ordered and disordered distribution is even more pronounced.

It follows from these numerical examples that if the arrangement of molecules is determined by chance, then the most "widespread", most easily achieved and most probable is a completely isotropic distribution with macroscopically uniform density, i. e. perfectly disordered distribution.

Under its external conditions, the most probable state of a gas is disorder, i. e. the state which can be achieved in the maximum number of ways.

2. Tendency Toward Disorder

Hence, if molecules are "left alone", if no forces hinder their thermal motions, then the most probable is a disordered, or random, distribution of the molecules.

Does this imply that spontaneous deviations from disorder are improbable? Does it follow that a "tendency" to disorder exists? Yes, it does.

To make this clear, we ask the reader two questions. The first is: Can we freeze water by heating it? Of course we cannot, the reader answers. But why not? On the face of it the question

seems absurd, but is it really so? In each special phenomenon we search for manifestations of the general laws of nature with which the material world around us complies. What law of nature "forbids" spontaneous freezing of water by heating? Maybe it is the law of conservation of energy? No, this law can be adhered to in the senseless process we are dealing with. We can conceive of a vessel of water placed on a heavy metal plate heated, for instance, to 300°C . Then we raise the temperature of the plate to 400°C and the water in the vessel freezes. The law of conservation of energy is not violated by this impossible event. The water gives up heat which is transferred to the plate.

Hence, the impossibility of the phenomenon described above must be based on something else.

Consider the molecular mechanism of heat transfer. We know that in a hotter body the molecules move faster than in a colder one. Let us bring two bodies having different temperatures into contact. Now, on an average, the slower molecules of one body begin to collide with the faster molecules of the other body. We find that after a certain time has passed, the result of these collisions is an equalization of the average velocities of the molecules in the contacting bodies.

Let us now describe the molecular state of the two contacting bodies before and after their temperatures are equalized. If a box contains white and black balls, their distribution is disordered when the probabilities of taking out a white or black ball are the same at any place in the box. But we already know that order and disorder may be realized with respect to any feature (recall, for instance, magnetic order). Therefore, we can also speak of order and disorder in the values of the average velocities of the molecules. A disordered state is one in which the average velocities of the molecules are the same at all points of space.

Thus, from the point of view of molecular physics, two bodies heated to different temperatures and in contact with each other do not constitute a system with a disordered distribution of its particles.

We can conclude that the transfer of heat from a less heated body to a more heated body is a transition from disorder to order. But the disordered state is the most probable one. This means that a transition from disorder to order is a transition from a more probable state to a less probable one. This is why such processes are usually not observed.

The second question is just as clear as the first. Can a flywheel start to rotate "by itself"? Of course not. To turn a flywheel

you require energy. Now just imagine that a flywheel starts to rotate and the temperature in the room in which your "machine" is located starts to drop. Here the mechanical energy required to rotate the flywheel does not simply appear out of nowhere, but is generated from heat. As far as the law of conservation of energy is concerned, there is nothing senseless in this phenomenon.

The impossibility of obtaining mechanical energy by cooling the environment is not at all obvious. Many inventors have spent their time and efforts in designing an engine operated by cooling the water of the oceans. What an alluring prospect! There is about one thousand million cubic kilometres of water on the earth. If we could cool all this water by only one-thousandth of a degree and utilize this evolved heat, we could produce a thousand million million kilowatt-hours of energy. A million million kilowatt-hours of electric energy is quite sufficient for the annual consumption of the whole world. Consequently, a negligible, entirely imperceptible cooling of the oceans, if it could be made use of, would provide all of mankind with an amount of electric energy that would easily meet the requirements of the next thousand years.

Alas, we cannot design such an engine. It is impossible, unfortunately, to rotate flywheels and to drive machine tools simply by cooling our environment. It is impossible because the process of a spontaneous transformation of heat into mechanical energy is improbable.

Lowering the temperature of the environment involves a reduction in the energy of chaotic, random motion of the molecules. To drive turbines or transmissions at the expense of this cooling operation entails the transformation of the energy of disordered motion of the molecules of the environment into energy of fully ordered motion of atoms of metal.

Again we find that the transition from disordered arrangement of the molecules into an ordered arrangement is impossible.

Hence, the thermal motion of molecules tends to disorder in their arrangement and to disorder in the directions of their velocities.

We dump a sack of black grains into a box, and then add a sack of white grains. Then we take a spade and begin to stir the white and black grains. The grains mix like the molecules do as a result of thermal motion. Soon the grains become so well mixed that if we grab a handful at random, we find we have about an equal amount of white and black grains. Order has been transformed into disorder. No matter how long

we keep stirring the grains, we will never sort them out so that the black and white grains are separated again. On the contrary, a more or less uniform distribution of the grains, black and white, is the stable state. With respect to molecules, such a state is said to be thermal equilibrium. In this state, the velocities of the molecules of a gas are distributed according to Maxwell's law (see page 18) and have no preferred directions of motion.

The tendency to disorder in the arrangement of molecules explains many phenomena discussed above and, primarily, the diffusion process.

What makes the molecules of a lump of sugar, thrown into a glass of tea, move upward (even though the molecules of sugar are heavier than water molecules) and mix uniformly with the tea? Their tendency to disorder. What makes atoms of zinc impregnate copper when plates of these two metals are pressed firmly together? Again, the tendency to disorder.

If we ignore this law of nature, phenomena associated with phase transitions and with phase stability are beyond our comprehension. If the molecules of a substance are not subject to the action of forces, their arrangement is disordered. If the molecules of a substance can adopt any of several arrangements, preference is given, all other things being equal, to the arrangement that provides thermal motion with more "elbowroom", and that enhances the tendency to freest, i. e. most disordered, motion.

3. Tendency Toward Order

How would atoms of matter be arranged if there were no thermal motion? This is no idle question, nor a scholastic one like "how many devils can be accommodated on a pinhead?". Thermal motion ceases at the temperature of absolute zero. To answer the question put at the beginning of this paragraph, we should describe how atoms are arranged at the temperature of absolute zero.

Exclusive features of the atomic world are due, to a great extent, to the existence of thermal motion. If there were no thermal motion, the laws of the atomic world would be similar to those of the world of large bodies.

Let us leave the world of atoms for the time being to find the conditions under which large bodies are in a state of stable equilibrium.

Equilibrium is attained when the sum of the forces acting on a body equals zero. A body is in equilibrium when the

force pulling it to the right equals the thrust to the left; when the downward pressure is equal to the upward reaction of the support on which the body rests.

Not every equilibrium, however, is stable. Just try to place a pingpong ball on the rounded shade of your desk lamp or stand an egg, small end down, on the table (without, however, resorting to Columbus's famous technique). It would seem that we can find a position in which the weight of an item is counterbalanced by the support reaction. Practically, you find it possible to attain such unstable equilibrium only for a moment.

When is equilibrium stable? For a ball, the answer is simple. You must put it into a hollow. The reason for its stability is that you must roll the ball to a higher position in order to get out of the little pit, i. e. you must do work against gravity. Consequently, the ball will not by itself roll out of the hollow because the work required cannot come from nowhere. The stable position of the ball in the pit is ensured by the law of conservation of energy.

If we carefully examine all cases of stable equilibrium, we will see that the reason for the stability is always the same. A sign of stable equilibrium is the necessity to perform appreciable work to disturb this state.

A suspended pendulum is in a stable position because work against gravity is required to displace it. A heavy suitcase lies stably on the spring mattress in the berth of a Pullman sleeping car. The weight of the suitcase depresses the mattress in the middle of the berth. You must do work to change the position of the suitcase: against gravity to move it upward, or against the elasticity of the mattress springs to move it downward.

The degree of stability in equilibrium may vary widely. A ball in a shallow depression and a ball in a deep pit are both in stable equilibrium. But not much work is required to roll the ball out of the depression, while a great deal may be needed to get it out of a deep pit. The degree of stability is evaluated by the depth of the "pit" in which the body is located.

Shown in Fig. 76 are two balls compressing a coil spring. Compression is maintained by a rubber cord attached to the balls. The cord is stretched, of course, and if the toy is in equilibrium, the tensile force of the rubber counterbalances the repulsive force of the compressed spring. This equilibrium is stable. To disturb it, i. e. to stretch the cord additionally or to compress the spring additionally, work must be done externally on the system.



Fig. 76. Two spheres in equilibrium.

The degree of stability of this equilibrium depends upon the strength of the rubber cord and of the steel spring. The work done in rolling the ball out of the depression in the first example coincides here with the work required to rupture the rubber cord.

Of interest is one general property of bodies or groups of bodies in stable equilibrium: such bodies can vibrate, or oscillate, about their equilibrium positions.

By deflecting the pendulum slightly from its vertical position, flicking the ball in the depression or pressing the balls connected by a spring and rubber cord together for a moment with one hand, we can initiate such vibrations. If there were no friction, these vibrations would continue without end.

Next we obtain a large number of balls, springs and rubber cords. Then we attach six hooks to each ball and connect the balls together with springs and cords, as illustrated in Fig. 77, where the position of stable equilibrium of the balls is shown.

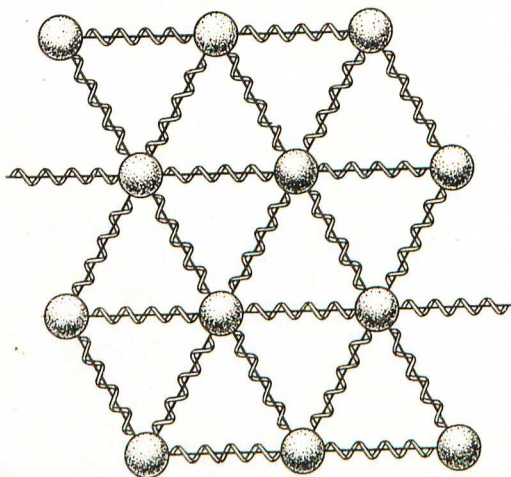


Fig. 77. "Closest packing" in a layer. The spheres are in equilibrium.

The centres of the balls are arranged as in a close packing arrangement of spheres.

The fact that stable equilibrium leads in our case to long-range order is so obvious that the reader will hardly demand a rigorous proof. If all the balls, springs and cords are identical, then any distortion of the illustrated regular arrangement requires work to compress the springs additionally and stretch the cords additionally.

But let us return to the world of atoms.

There are forces of attraction (rubber cords) and of repulsion (springs) acting between atoms of matter. These two kinds of forces are, of course, of different nature. Forces of interaction between atoms are of electrical origin. We cannot dwell here on this question; it cannot be adequately explained in a few words and a detailed discussion would take up too much space and is beyond the scope of the subject. Only one point is essential to our discussion: at great distances the atoms are subject to forces of attraction (the cord is stretched, the spring is not compressed); as the atoms come closer together, attractive forces decrease and repulsive forces increase. Finally, there is an instant of stable equilibrium: attraction and repulsion equal each other.

A substance consists of a huge number of atoms. What mutual arrangement of the atoms is the most stable? The model with the balls has already answered this question. Long-range order in the arrangement of the atoms of a substance is the most stable arrangement. The tendency toward order is a manifestation of the same law that makes a ball roll down a hill and rest in a hollow. It is the tendency toward a position of stable equilibrium.

4. Order Versus Disorder

We have found that the most probable distribution of molecules is one of disorder both with respect to their arrangement and with respect to the directions of their velocities.

As to the magnitude of the velocities, disorder is manifested as maximum freedom of motion. With gases, this maximum freedom of motion leads to Maxwell's distribution of velocities. But when forces begin to act on the particles an entirely different picture emerges.

The action of forces is directed toward establishing order. When atoms (or molecules) are in thermal motion and are subject to the action of forces, the most probable distribution

of particles is no longer disordered and the distribution of their velocities is no longer Maxwellian.

The struggle of order against disorder can be observed in numerous examples. Almost all of the data presented in the preceding chapter illustrate this vital law of nature, this unique balance of two tendencies: toward order, i.e. toward stable equilibrium, and toward disorder, i.e. toward the most probable distribution of particles in thermal motion.

A very simple and typical example is the distribution of molecules in a vertical column of air.

If there were no thermal motion, the tendency toward equilibrium would force all the particles against the earth's surface.

How are the particles actually distributed? It is well known that the pressure and, consequently, the density of the air decrease with an increase in altitude. Over each 5.6 kilometres of altitude the air density is reduced by half. This striking example demonstrates a compromise between the two tendencies. When the forces of gravity exist, complete disorder, i.e. perfectly uniform density, is no longer the most probable state.

From this point of view, it is quite clear why a gaseous (disordered) distribution of particles is most probable under certain conditions, why the formation of short-range order is most probable under other conditions, and why long-range order in the arrangement of the particles is set up under a third set of conditions.

At the highest temperatures, molecules have high velocities. The forces of interaction between the molecules have no appreciable effect, at such velocities, upon the arrangement of the molecules. As the temperature drops, the average velocities of the molecules also decrease. Finally, the time comes when the cohesive forces begin to assemble the atoms (or molecules) into drops. The most probable under the new conditions is short-range order in the arrangement of the particles.

Upon a further drop in temperature, there is a time when the vibration of the atoms has slowed down sufficiently for them to form a regular space lattice. Under these conditions, long-range order is the most probable arrangement of the particles.

The transition from the liquid to the solid state can be visualized by means of the following model. Imagine an open box with shallow spherical hollows in the bottom. The box is filled with a single layer of balls. The hollows are aligned in regular rows and form a network. The number of hollows equals the number of balls.

We begin by continually shaking the box. The balls roll about at random, executing small oscillatory motions in the hollows and then popping out of them. All in all, they display a typical "liquid" picture, like that discussed above. Next we begin to slow down the oscillations of the box. The time comes when a ball that gets into a hollow cannot get out again. Continuing to shake the box without changing the intensity of oscillation (to simulate a constant temperature), we ultimately reach a point when each ball has found its hollow (a crystal has been formed).

If we rapidly reduce the oscillations of the box, only a few balls find their hollows. As a result, no crystallization occurs; the same liquid picture, typical of amorphous solids, remains when we stop shaking the box.

Hence, at small oscillations of the box with the hollows, the most probable is an ordered arrangement of the balls — a crystal lattice. If the hollows are very shallow, a situation may exist for an extremely long (practically unlimited) length of time in which a part of the hollows are occupied by balls and a part of the balls roll about, either eluding the hollows or not lingering in them. In this model we perceive order with elements of disorder. Consequently, if the probabilities of an ordered and a partially disordered state differ only slightly, then order and disorder coexist.

In what way can two different phases of a substance be in equilibrium?

Consider, for example, a crystal and saturated vapour. The state of the crystal — long-range order — is stable. Work is required to detach a particle from the crystal and to transform it into vapour. It would seem that the state of the vapour is less stable. Nevertheless, the two phases are in equilibrium.

What compensates for the lower stability of the vaporous state? The tendency toward order is realized in the crystalline arrangement of the atoms. The tendency toward disorder, however, is repressed in the crystal. The atoms are crowded, their motion is hindered. In vapour there is much more volume per particle. Thermal motion has more elbowroom; it acquires utmost freedom. The tendency toward disorder is gratified.

We can say that equilibrium of a crystal and vapour requires that the "sum" of the order and disorder be the same for both phases. The higher the order in the crystal, the greater the disorder should be in its saturated vapour.

We know that saturated vapour has different pressures at different temperatures. The lower the temperature, the lower

the pressure and, consequently, the density of the saturated vapour. If the density is lower, the volume available per molecule is greater, as is the degree of freedom and, thereby, the disorder in the vapour. Since a crystal is compressed only slightly with a drop in temperature, the volume available per atom and, consequently, the degree of disorder of the crystal vary but little. On the contrary, the degree of stability (tendency toward order) of the crystal increases: the lower the temperature, the greater the work required to detach a molecule (or atom) from the crystal.

When we change the conditions of equilibrium between saturated vapour and a crystal, we find various compromises between order and disorder. If there is much disorder in one phase nature compensates with more order in another phase.

By violating the conditions of equilibrium, for instance by raising the temperature without changing the pressure, we can sublime the crystal. The tendency toward disorder takes the upper hand. The thermal motion of the particles becomes so intensive that the gain in the stability of the crystal cannot withstand it.

What happens in phase transitions in solids? Returning again to the model of the balls rolling about in a box with hollows in the bottom, we can contend that the difference between the two phases can be likened to the depth of the hollows. One of the phases is more stable.

But how then can two phases exist in contact? Here again, stability, i. e. tendency toward order, is compensated for by the tendency toward disorder, i. e. the availability of more freedom provided by nature for thermal motion.

At a high temperature, the role played by disorder becomes more significant and the more probable is the phase with the wider, rather than the deeper, "hollows". In other words, the atoms require more volume in which they can move. Therefore, the feasible solid phase at high temperatures is the one in which the atoms are bonded with one another more weakly and can vibrate more intensively.

When the wide "hollows" are also the deeper ones, i. e. if the more stable phase is also the one that provides more freedom for the vibration of the atoms, then such a phase is stable always and under any conditions.

It is a different matter when phase transitions occur. Here the hollows of one phase are narrower, but they are also deeper.

The condition of equilibrium for two such phases evolves

when the opportunity for thermal motion (tendency toward disorder) in one of them is compensated for by the greater stability (tendency toward order) of the other phase. If we raise the temperature, disorder prevails. If we lower the temperature, the tendency toward stability (toward order) leads to the corresponding phase transition.

5. In All Fields of Knowledge We Find Problems of Order and Disorder

We have completed our discourse on the role of order and disorder in the structure of matter. We feel, however, that it is too soon to finish our discussion at this point.

Several years ago the author received a letter from a reader. It was a touching letter, both naive and serious at the same time. The reader suggested that the author write a new book — on order and disorder in the world of people — about how to combat diseases and unemployment, to fight for peace and against pollution of the environment, against all the abnormal phenomena originated by capitalism and the demographic explosion. “All of these phenomena”, this reader quite correctly contended, “are none other than problems of disorder in the world of mankind.”

I answered the reader that such books are written by many journalists, news commentators and students of political science; such writing is beyond my powers. My forte is writing about science. A part of my profession is to write about the complex ideas of today's science in terms understandable to the layman.

But, on the few pages that close this book, I should like to touch upon the problems of order and disorder in other fields of science. Probability theory and statistics are truly versatile tools applied literally in all sciences. Our subject was order and disorder in the world of atoms. But how similar are the problems we treated to those facing investigators working on the theory of games, on the distortion of information in radiobroadcasts, as well as those studying the laws of heredity or employing methods of probability theory in sociological research.

Let us dwell briefly on these problems, if only to demonstrate that the problems we discussed are only a part of the scientific approach to random phenomena. There are so many topics illustrating this idea that I hardly know what to begin with.

We discussed the errors that occur in stacking layers of atoms in building up a crystal. This problem appears to have much in common with errors that occur in transmitting information.

A perfectly correct sentence, such as "Arriving on Wednesday" corresponds to complete order. If the transmitting (or receiving) apparatus is out of order, this correct sentence may be transformed into "Arriwing on Wednesday" or "Arriving on Nednesday". Such distortions constitute elements of disorder in order. We can evaluate their probability and contend that in such an amount and of such a kind, these errors cannot prevent us from understanding the meaning of the telegram.

Distortions, however, which transform this sentence into the combination of words "Arriving on wedding day" are equivalent to a polymorphic transformation. The initial structure is completely lost and the meaning of the sentence has been altered.

Another example. The emergence of elements of order in disorder, which we illustrated in such detail in describing the structures of liquids and solids, has much in common with the vital problem facing radiophysicists in their effort to raise the level of the signal above that of the noise.

If you turn on a transistor radio and try to tune in on a distant station, you will hear noise. It will be difficult to make out the words. Assume that the broadcast we wish to tune in on is simple to the extreme: a weak signal is repeated after definite time intervals. But if the strength of the signal is too low, it is drowned in the noise.

This would seem to be a hopeless situation: disorder has overcome order. But now assume that a recording apparatus has been connected to our receiver. The stylus traces a disordered zigzag curve. Imagine that we continue repeating the recording of the noise over lengths of time exceeding the intervals between the signals. This leads to the following. The signal is recorded at the same place on the chart. If we repeat our interval a thousand times, the signal is enlarged by a thousand times. How about the noise? It also grows, of course. But since the noise is disordered and random, its peaks often coincide with its valleys. It can be proved that the noise increases with the square root of the number of times the interval is repeated. Hence, in principle, if we have ample patience, we can "fish order" out of any kind of disorder.

We shall dwell in a little more detail on another example. Let us compare the behaviour of binary alloys with problems of genetics. The kind of structure obtained in mixing together two substances that form a solid solution depends upon the interaction between the atoms. Of cardinal importance are the interrelations between the interaction energies of the atoms of the

first kind between themselves, of the atoms of the second kind between themselves, and of the atoms of the first kind with those of the second kind.

In what way does this phenomenon resemble the birth of a new being? In that here as well we deal with the formation of a new structure from particles, the so-called genes.

A living organism contains a great many genes. Each gene is responsible for a single inheritable characteristic. There is, for instance, a gene for blue eyes or a gene for a long nose or one for a quarrelsome disposition. Each gene has its opposite gene and they exist in pairs in the organism. For the blue-eyes gene, this is a hazel-eyes gene, for the long-nose gene it is a short-nose gene and for the gene of a quarrelsome disposition it is one for an obliging disposition.

To clear up the facts in a simple way it is necessary to assume that the genes in the organism go only in pairs. Then there may be individuals who have a pair of identical genes for a certain inheritable characteristic, say two blue-eyes genes, and also individuals that have pairs of opposite genes. Thus, speaking of eye colour, we find individuals with a pair of blue-eyes genes, with a pair of hazel-eyes genes and with a pair of opposite genes (one blue-eyes and the other hazel-eyes).

If both genes are of the blue-eyes type, the eyes of the new individual are blue, of course; if both are hazel-eyes genes, the eyes are hazel. But what happens when one gene is of the blue- and the other of the hazel-eyes type?

This question is answered by the following law. Of the two opposite genes, one suppresses the other. The one who gains the upper hand is said to be dominant and the one who gives way, recessive.

The problem of the gene "content" of an animal or plant, and that of the dominant gene of a pair of genes can be solved only by experiment. That the leading role in the determination of eye colour is played by the hazel-eyes gene I know from my own experience. I have three children and they all have hazel eyes. None of them has inherited my bluish-grey eyes.

As a matter of fact, we have not yet discussed how hereditary characteristics are transmitted from one generation to the next. The daughter organism picks each pair of its genes from two pairs, those of the father and mother, according to the laws of chance. When dealing with a gene which may be present in either the form B or the form H, the following combinations for transmitting the hereditary characteristic are possible:

Father	Mother	Children
BB	BB	BB
BB	BH	$\frac{1}{2}BB + \frac{1}{2}BH$
BB	HH	BH
BH	BB	$\frac{1}{2}BB + \frac{1}{2}BH$
BH	BH	$\frac{1}{4}BB + \frac{1}{2}BH + \frac{1}{4}HH$
BH	HH	$\frac{1}{2}BH + \frac{1}{2}HH$
HH	BB	BH
HH	BH	$\frac{1}{2}BH + \frac{1}{2}HH$
HH	HH	HH

The last column shows the pairs of genes transmitted to the children.

This table only enables us to assess the probability of events and cannot be used for sure prediction of them. It follows, for instance, from the table that a hazel-eyed father with the gene formula BH and a blue-eyed mother with BB may have either a blue- or a hazel-eyed offspring, the chances being equal. Can there be five blue-eyed children in this family? Of course there can and the probability of this event is the same as the same colour coming up five times in a row in playing roulette. This equals one-half to the fifth power: one thirty-second.

The founder of modern genetics, the Austrian monk and botanist Gregor Johann Mendel (1822-1884), conducted a huge number of experiments in crossbreeding plants with different characteristics. These experiments became the basis for formulating the model of transmission of hereditary characteristics described above. Since the number of "offspring" in these experiments was in the hundreds and thousands, the laws of probability were manifested with sufficient distinctness.

Consider, for example, this experiment. If we cross a pea plant having smooth-skinned peas with one having wrinkled peas, the next generation of plants all have the same kind of peas: all the offspring have smooth-skinned peas. This means that according to our model a smooth skin is the dominant characteristic. Looking into our table, we find that the features of the posterity of the two kinds of pea plants correspond to the third line in the table. The parents should have the gene pairs SS and WW and the children, pairs of genes SW, with S for smooth-skinned and W for wrinkled gene.

To check the validity of the model, we then cross the offspring with one another. The probability formula for the third generation is $\frac{1}{4}SS + \frac{1}{2}SW + \frac{1}{4}WW$. Since S is the dominant characteristic, the probability of obtaining smooth-skinned peas is $\frac{3}{4}$, and that of wrinkled peas is $\frac{1}{4}$. Hence, as we increase the number of experiments, the ratio of the number of "smooth" grandsons and granddaughters to the number of "wrinkled" ones should approach three. In one of his series of experiments, Mendel found the numbers 5474 and 1850, the ratio being equal to 2.95. The deviation from the theoretical value is less than 2 per cent.

I think the reader will agree with me that this phenomenon is a special case of order with elements of disorder (it would be perfect order if the ratio equalled exactly three).

Many novelists have written, at some time in their careers, that they could not cope with the heroes of their novels. When he started to write, for instance, the novelist intended to finish his book triumphantly for his hero. But the logical trend of events and interplay of the characters led to a situation in which the hero ended up a complete failure. I must confess that I too, in my books on science for non-scientists and publicistic writings, do not always finish a book as I had intended to when I outlined my plans. I began this book by describing the gaseous state of matter. In the chapter called "Disorder", I portrayed the molecular structure of a gas. If I had stopped at that point, all would be quite logical. I continued the chapter, however, by telling about the velocity distribution of molecules. But this distribution fully complies with a law! And near the end of the book we learned that whatever complies with a law of nature can be called ordered. Though the velocities of molecules do not lead to microdisorder, they met the requirements of macroscopic order. But macroscopic order *is* order!

Therefore, any event in the world of large numbers that obeys the laws of probability theory can be regarded as a manifestation of order with elements of disorder. Heredity is only one of the countless number of examples.

It can be convincingly proved (and the author has tried to do this in another book*) that we find such order in the humanities as well, and not only in studying dead matter. Opinions of judges on sport events (evaluated in points, as gymnastics and

* *The Improbable Is No Fact*, Molodaya Gvardiya Publishers, 1972 (in Russian).

figure skating), and the concepts of good and beauty, and many more ideas of this kind have macroscopic order.

The author would even risk contending that deviations from artistic truth in the literary works of poor writers can also be regarded as an essential departure from order.

It follows that if we wished, we could easily go over from our subject of order and disorder in the world of atoms to the vital problems of order and disorder in the world of mankind.

One of the fundamental principles of dialectical materialism is the statement that there is a single approach to physical, biological and social phenomena. The laws of probability and the rules of order and disorder constitute an important element in this general scientific approach.

TO THE READER

Mir Publishers would be grateful for your comments on the content, translation and design of this book. We would also be pleased to receive any other suggestions you may wish to make.

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QUASIPARTICLES

M. KAGANOV, D. Sc. and I. LIFSHITS, Member, USSR Acad. Sc.

This book does not contain mathematical formulas or deductions. The entire treatment has been built up on analogies by the authors, on the assumption that the reader possesses a flair for physics. One can learn from this booklet how the atomic particles move in solids, what lies behind the term "thermal motion", and how the nature of movement of atomic particles is manifested in macroscopic properties of solids.

The booklet is intended for a wide circle of readers.

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This book is written for the layman, and it is written in a simple easy-to-understand manner. Moreover, there are numerous drawings to help the reader to better understand the material.

Both authors concentrated their immense talents on simplifying and making understandable such normally complex ideas as the atomic structure of matter, theory of lunar tides, theory of shock waves, theory of liquid helium, and numerous other theories.

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ALEXANDER
KITAIGORODSKY, D. Sc.
(Phys. and Math.), graduated
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The Structure of Matter,
*The Atomic Nucleus, Physics
for Everyone* (with Lev Landau
as co-author), *I am a Physicist*,
Renyxa, *The Improbable Is
No Fact*, etc. His articles
on the creation of new substances
and materials of the future
were published in the
collection *Things to Come*.

The present book deals with
the solid, liquid and gaseous
states of matter.

One of its winning features,
however, is that problems
of structure are considered
from a definite point of view,
as a manifestation of the
peculiar struggle between
Order and Disorder in
the atomic world. In his
treatment of these combining

forces, the author was able
to discuss, in addition to
the fundamentals of the atomic
structure of matter, a multitude
of technological processes,
highly significant in our day,
such as the conversions that
occur in plastics and rubbers,
or the annealing and plastic
working of metals.

Neither did Professor
Kitaigorodsky ignore problems
concerning living tissues.
Here again he finds that this
unique mixture of order and
disorder in the arrangement of
biological molecules is of
primary importance in
understanding the laws of
molecular biology.

The new, fifth, Russian edition,
from which this translation
has been made, was revised
and supplemented with much
important up-to-date material.

Owing to its simple language
and exposition, this book will
be of interest to readers
acquainted with only the
fundamentals of physics.